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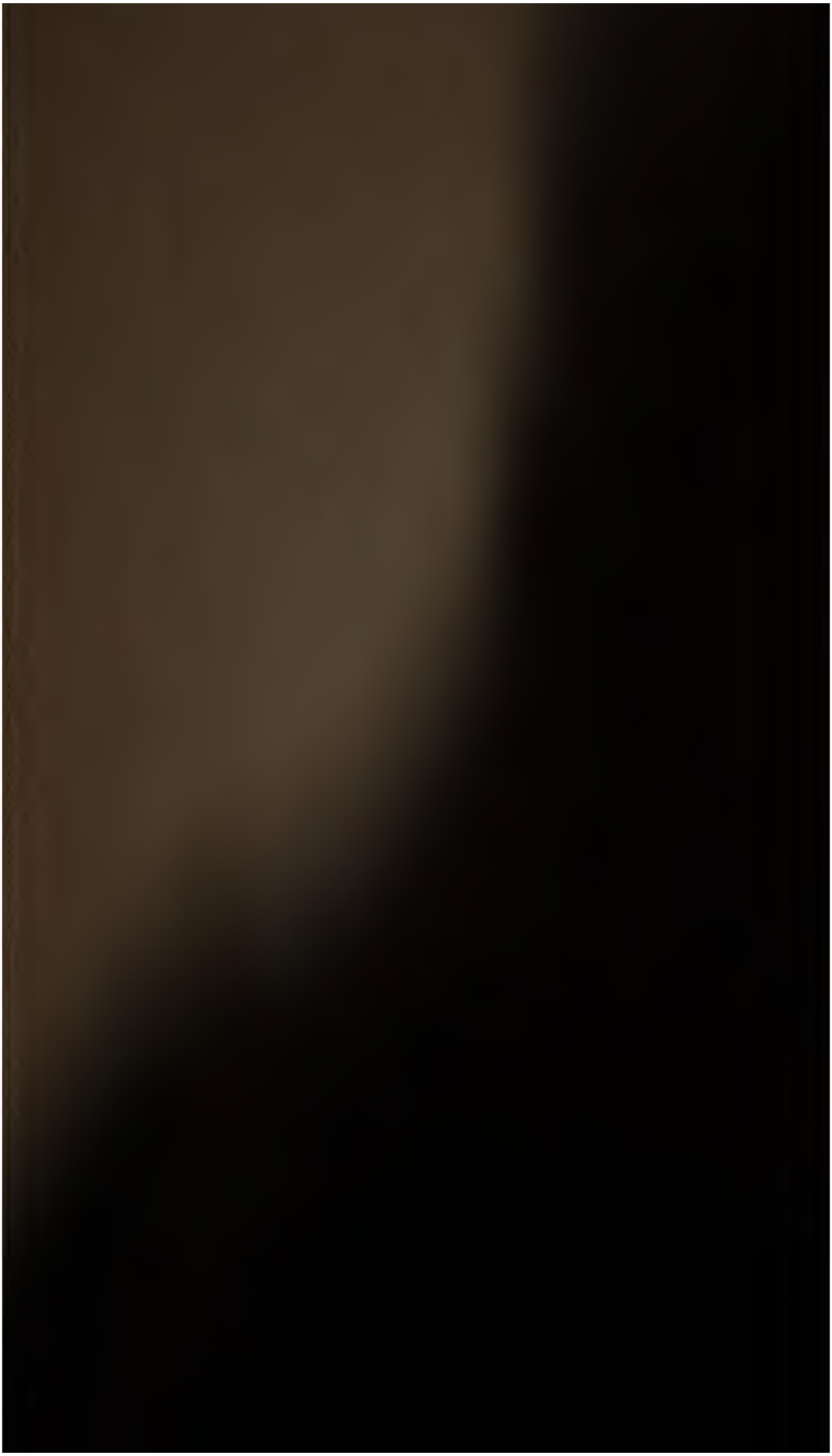

HINRICHS'

PRINCIPLES OF CHEMISTRY

AND

MOLECULAR MECHANICS.

The form, dimensions, and motions of the chemical molecules, are determined by the thermometer and the goniometer — as the form, dimensions, and motions of the planets are determined by the pendulum and the theodolite.

THE PRINCIPLES

OF

PHYSICAL SCIENCE,

DEMONSTRATED BY

THE STUDENT'S OWN EXPERIMENTS

AND

OBSERVATIONS,

BY

DR. GUSTAVUS HINRICHS.

IN THREE VOLUMES.

VOL. II.

THE PRINCIPLES OF

CHEMISTRY AND MOLECULAR MECHANICS

DAVENPORT, IOWA, U. S.:
DAY, EGBERT, & FIDLAR.
NEW YORK: B. WESTERMANN & CO.
1874.

THE

PRINCIPLES OF CHEMISTRY

AND

MOLECULAR MECHANICS,

BY

DR. GUSTAVUS HINRICHS,

Professor of Physical Science in the State University of Iowa. Member of
several Scientific Societies of France and Germany.

WITH TWO PLATES.

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PREFACE.

THIS volume is submitted to the scientific public as an introduction to *Molecular Mechanics*, and to the student as a guide in the study of the general *Principles of Chemistry*.

The more general results of nearly twenty years' labor in molecular mechanics, are here for the first time presented in logical continuation of what but too often is termed "modern chemistry." It is hoped that this method of exposition will lead to a more generous recognition of mechanics by chemists, and tend to open new and promising fields of research.

We trust that the student will find this book not only a safe guide, teaching nothing new that has to be unlearnt, but also a profitable guide, leading him up to those higher principles from which the best view of the field of facts can be enjoyed.

Formerly, in the absence of general principles, general methods of operation, and general laboratory practice, there was some reason for the striking similarity between cook-books and chemical treatises for students. Now, the general student, having practiced the *Elements of Chemistry* in the laboratory, can profitably master a work so unlike a cook-book as the present volume. The hints here given for work will be amplified in the laboratory in those cases which the student may want to practice. Thus, the *method* of research and of scientific verification will be fully acquired — without consuming all the time at disposal for the *science* of chemistry in the enumeration of dry, and yet insufficient, details of operations not understood.

Full collections of compounds, models, charts, etc., etc., are, of course, necessary, where this book is used in colleges or universities.

May this book, the result of many years of thought and work, be useful in the cause of science.

ORIGINAL CONTRIBUTIONS TO MOLECULAR MECHANICS CONTAINED IN THIS VOLUME.

---

1. *Graphical and Stereographical Formulæ.*
2. *Rotation of Molecules.*
3. *Moment of Inertia of Molecules.*
4. *Motions of Molecules in the three States of Aggregation.*
5. *Specific Heat of Vapors.*
6. *Molecular Volume of Liquids* (Alcohol Serials).
7. *Boiling Point of Serials.*
8. *Boiling Point of Isomers.*
9. *Determination of Chemical Constitution* (*Form*) *by the Thermometer.*
10. *Determination of Molecule of Binaries and Ternaries.*
11. *Determination of Crystal Form from Molecule.*
12. *Selection of Crystal Symmetry.*
13. *Molecular Perturbutions.*
14. *Classification of the Elements..*
15. *Stas' Determinations as Secondary Perturbations.*
16. *Atomic Weight and Atomicity of Elements Calculated from General Constitution.*
17. *Co-ordinates of Atoms in Molecule.*
18. *Law of Pressure, in Ebullition and Dissociation.*
19. *Law of Probability Regulates Dissociation* (Elementary Demonstration).
20. *Law of Probability Regulates Chemical Velocities.*

For additional contributions, see Chronological List of Publications, at the close of this volume.

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HINRICHS'
GRADED COURSE IN PHYSICAL SCIENCE.

[illegible] by the Student's own Experiments and [illegible].

FIRST GRADE — The Rudiments of Physical Science — *For Grammar Schools.*

(One volume, in three parts — in preparation.)

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VOL. II. — THE PRINCIPLES OF CHEMISTRY AND INTRODUCTION TO MOLECULAR MECHANICS (*this volume*). 1874. Price, bound, $2.50.

FOURTH GRADE — Special Treatises for Advanced Students of Physical Science.

THE PRINCIPLES OF PURE CRYSTALLOGRAPHY. (Published 1871.) Price, paper, 50 cts.

CONTRIBUTIONS TO MOLECULAR SCIENCE — Nos. 1 to 4. (Published 1868-69.) Price, paper, 50 cts.

QUALITATIVE CHEMICAL ANALYSIS. (In preparation.)

URINE ANALYSIS AND TOXICOLOGY. (In preparation.)

The above volumes, as far as published, will be sent, prepaid, to any part of the United States, by remitting the price to

DAY, EGBERT, & FIDLAR, PUBLISHERS,
DAVENPORT. IOWA.

INTRODUCTION.

1. *The Principles of Chemistry* here to be presented, comprise a concise exposition of those *general principles and laws of the science of chemistry* which should be understood by all who pretend to a liberal education. Hence the specialties, of however high an importance to the specialist, whether in pure chemical science or its innumerable applications, cannot find a place in this volume.

2. The subject of this treatise will be presented in three parts:

Part first will treat of the general principles of *theoretical chemistry*, giving the general laws of chemical processes, the formulæ representing the compounds, and the physical phenomena manifested during their formation.

The second part will contain a concise synopsis of *systematic chemistry*, comprising a short description of the most important chemical compounds, in systematic order.

The third part treats of the general principles of *applied chemistry*, enabling the student to understand the principal processes of the chemical arts.

3. For the sake of clearness and brevity, the results obtained by the chemical investigators will be *stated* in as few words as possible, and thereafter *experiments* will be described whereby the student can verify the truth of these statements.

4. Either the inductive or the deductive method would have been more scientific, perhaps; but the aim kept in view during the preparation of this work was not so much a theoretically finished treatise, as a *guide* to students who, in the lecture-room and the laboratory, desire, at the expense of comparatively a short time, to become thoroughly familiar with the general principles of chemistry. At the same time, the author is confident that this little volume will give those students who expect to study *any branch* of chemistry as a specialty, exactly that preparatory training which will facilitate their special work.

5. It is expected that the student, before taking up this volume, has mastered our "*Elements of Physics*" and our "*Elements of Chemistry*," to the *articles* of which we shall frequently refer, under the abbreviations "Phys." and "Chem." Thus, Phys. 18–20, refers to the proper method of weighing, as treated of in articles 18 to 20 of the Elements of Physics.

6. It is not *necessary* that the student should complete our "*Method of Quantitative Induction*" before studying these principles of chemistry. Nevertheless, we cannot too strongly recommend that study, on account of the training it necessarily yields. At any rate, it will be proper here to accept the results of the experimental researches contained in that work. We shall cite it as "Induct.," adding the number of the article of that work referred to.

7. In some cases, it is not readily possible for the general student to verify a given chemical principle by his own experiment; in such cases, reference will be made to descriptions of the experimental researches, whereby the principle was originally established.

8. It was *not* the intention of the author to furnish a reading book on chemistry, but a faithful and useful *guide* to the student; hence, brevity will be studied—it being supposed that the *teacher* takes this book simply as a *text* for his lectures, while the student makes use of the book in lieu of "*lecture notes*" and special laboratory "*instructions.*"

9. Some additional hints in regard to the proper use of this volume may be found in an *appendix*, to which the teacher is respectfully referred. Students who attempt to use this book without the assistance of a live teacher, will do well to study the same appendix before proceeding further.

10. It need hardly be stated that only metrical weights and measures will be referred to in this treatise, and that the degrees of temperature here always are expressed by the centigrade scale.

PART I.

THEORETICAL CHEMISTRY.

11. *Theoretical Chemistry treats of the general laws which govern the composition, structure, and reaction of substances,* without regard to the description of the individual compound, or their application and preparation in the arts.

12. The conception of a *chemical atom* is the basis of modern chemical theory. This conception must not be confounded with the philosophic idea of an atom as an *absolutely* indivisible particle of matter.*

Section I. Chemical Atoms.

13. *A chemical atom is a very minute, relatively indivisible, particle of matter.* A chemical atom of any compound is, accordingly, not absolutely indivisible; but, *if* divided, it will no longer be an integral part of the same compound, but it will have been divided into chemical atoms of a less complex compound. Thus, an atom of lead sulphide is relatively to *this* compound indivisible; but, if divided, it separates into an atom of the less complex lead and in an atom of sulphur.†

14. *A chemical atom has,* according to this definition, necessarily, *form, magnitude,* and *weight.*

---

* The chemical atom is a reality—the philosophic atom a possibility.

† This idea of *relative indivisibility* is not peculiar to chemistry—it applies to almost all things. Thus, a flower is indivisible, as such; when divided, we have only petals, stamens, etc. A book is relatively indivisible—when divided, we obtain only leaves, etc. As equal books constitute a library, so atoms constitute a body.

It is the object of theoretical chemistry to determine these properties for the atoms of all substances, and ultimately to deduce the properties of the substances from these properties of their atoms.

15. *The chemical atom of an element is represented by the symbol of that element;* thus, H represents one atom of hydrogen, O one atom of oxygen. (Chem. 110.)

16. *The chemical atom of a compound is represented by the formula of that compound.* Thus, H_2O represents an atom of water, composed of two atoms of hydrogen and one atom of oxygen. An atom of alcohol is represented by C_2H_6O, because it consists of two atoms of carbon, six atoms of hydrogen, and one atom of oxygen. Compare Chem. 184.

17. *The atomic weight of any substance is the number of hydrogen-atoms required to balance the weight of one atom of the substance.* Thus, $O = 16$, because it would require 16 atoms of hydrogen to balance the weight of one oxygen atom. In the same manner, $N = 14$, H_2O is 18, C_2H_6O is 46. (Chem. 182.)

18. The following *table of the atomic weights of the elements*, in alphabetical order of symbols, results from the latest determinations. (Compare Chem. 183.)

Ag	108	Cl	35.5	Li	7	Rh	104
Al	27.4	Co	60	Mg	24	S	32
As	75	Cr	52	Mn	55	Sb	122
Au	196	Cu	63.4	N	14	Se	79
Ba	137	Fe	56	Na	23	Si	28
Bi	208	Fl	19	Ni	58	Sn	118
Bo	11	H	1	O	16	Sr	87.6
Br	80	Hg	200	P	31	Te	128
C	12	Ir	198	Pb	207	Ti	50
Ca	40	Io	127	Pd	106	Ur	120
Cd	112	Ka	39	Pt	198	Zn	65

19. By means of this table, it is easy to *calculate the percentage* composition of any compound for which the formula has been given, and also to calculate the amount of the products formed in given chemical processes. Thus, the formula of blue vitriol is $Cu\,O_4\,S + 5\,H_2\,O$. Calculate how many per cent water, $H_2\,O$, will pass off; how many per cent copper sulphate, $Cu\,O_4\,S$, will remain when the blue vitriol dissociates at a temperature not far above the boiling point of water, and compare these theoretical results with those obtained according to your experiments (Chem. 93.) Also calculate the percentage of copper oxide, $Cu\,O$, and finally of copper, Cu, that will remain from the blue vitriol after ignition at red heat (Chem. 94) and reduction by blow-pipe (Chem. 95.)

Other good examples for calculation of percentage, are: the water of crystallization of *alum*, $Ka_2\,O_4\,S + Al_2\,(O_4\,S)_3 + 24\,H_2\,O$, and *gypsum*, $Ca\,O_4\,S + 2\,H_2\,O$, for which the amount has been determined experimentally according to Chem. 93.

The preparation of oxygen from potassium chlorate, $Ka\,O_3\,Cl$, leaving potassium chloride, $Ka\,Cl$; the preparation of hydrogen from Zn and dilute hydrogen sulphate, $H_2\,O_4\,S$, yielding $Zn\,O_4\,S$ and $2\,H$, enable the student te verify proportions given in Chem. 100 and 104. In the same manner verify the fractions used in Chem. 158, since the formula of water is $H_2\,O$, and that of carbon dioxide $C\,O_2$. Also calculate how much silver nitrate, $Ag\,O_3\,N$, must be taken to form a litre of a solution such that each cubic centimeter contains 3.042 mgr of silver; and how much chlorine will one cubic centimeter of this solution precipitate, if the resulting silver chloride has the formula $Ag\,Cl$? Compare Chem. 208.

20. The more carefully the experiments here referred to have been made, the more accurately will the results obtained by these experiments be expressed by the numbers calculated from the formula; accordingly, such experiments *verify* these formulae, and the atomic weights involved.

How the atomic weights are determined, and the formulæ established, will appear further on.

21. Since the weight of the atoms is expressed in that of a *hydrogen atom as unit*, the resulting figures really represent the *relative atomic weights* only (compare 17 and 18). For all practical purposes, these relative atomic weights are fully sufficient, since usually only the proportions of substances are of importance. Still, it is of a high scientific interest to know the *absolute* weight of the atoms.

22. *The absolute weight of one atom of hydrogen* is about one four hundred millionth of a millionth of a millionth of a milligram, or—

$$\text{H about } \frac{1}{400,000,000,000,000,000,000} \text{ mgr.}$$

In other words, one milligram of hydrogen contains about 400,000,000,000,000,000,000 atoms of hydrogen. (*Loschmidt;* see *Maxwell* in *Nature*, 1873, August 11.) Accordingly, a milligram of gold contains about 2,000,000,000,000,000,000 atoms. To obtain some kind of an idea of the vastness of this number, let us suppose that every human being on the face of the earth was a "millionaire," possessing a million of gold atoms, then one milligram of gold would furnish enough for the population of 2,000 such earths!

23. In order to express the minute atomic quantities more conveniently, the metrical system may be completed by a few additional units. It is already customary among microscopists to call 0.001 mm. a *micron*, and to denote it by μ. Accordingly, a *millimicron*, mμ, is the thousandth of a micron, or the millionth of a millimeter. The cubic-millimeter of water weighs a milligram; hence the cubic millimicron of water may be called a *microgram*, and denoted by μgr.* We shall then have—

$$1 \text{ mgr} = 1,000,000,000,000,000,000 \ \mu\text{gr.}$$

---

* It is evident that the microgram is to the milligram as the latter to the weight of a *cubic kilometer* of water.

Accordingly, we may now more concisely express the figures of 22 by saying that an atom of hydrogen weighs about $^1/_{400}$ of a microgram, and that an atom of gold weighs about $^1/_2$ of a microgram.

These minime metrical units will be useful in subsequent portions of this volume.

24. That the absolute weight of the chemical atoms is far below the thousandth of a milligram, may be proved by the *microscopic observation* of the crystals which form when a tenth of a milligram of the element crystallizes on the glass slide. More than one hundred distinct crystals will thus be obtained, and as each microscopic crystal necessarily contains a great number of atoms, the weight of each of these is a small portion of 0.001 mgr.

By dissolving one-fourth of a gram of any element to 100 cc solution, each drop of this solution will contain 0.1 mgr of the element, since one cubic centimeter contains about 25 drops. (Phys. 12.) Calculate from the chemical formula and the atomic weights of the elements, how much silver nitrate, $Ag\,O_3\,N$, must be dissolved in 100 cc in order that each drop of the solution will contain 0.1 mgr of silver? How much of lead nitrate, $Pb\,(O_3\,N)_2$, in order to obtain a corresponding lead solution? How much of potassium iodide, $Ka\,Io$, to obtain an equally strong iodine solution?

24*. The actual microscopic manipulations may now be performed in the following ways:

a. Spontaneous evaporation of *a single drop*, obtained by touching the slide with the glass stopper of the flask containing the above solutions; get crystals containing, in all, 0.1 mgr of the element.

b. Add a very *minute* fragment of a more soluble metal to the drop of the metal solution on the slide, and the less soluble metal will be set free by substitution. (Chem. 174.) Observe the reduction of silver nitrate by copper, lead nitrate by zinc, in strong reflected light! The crystals obtained are very numerous, forming most beautiful arborescent groups.

c. Put two drops of such solutions at a short distance one from the other on the slide, and draw one into the other by a small glass rod; by double decomposition (Chem. 203) often beautiful crystals are obtained. Thus, $\mathrm{Pb\ N}^{\underline{\mathrm{ate}}}$ and $\mathrm{Ka\ Io}^{\underline{\mathrm{ide}}}$ give beautiful hexagonal yellow* tablets of $\mathrm{Pb\ Io}^{\underline{\mathrm{ide}}}$; also acicular crystals of $\mathrm{Ka\ N}^{\underline{\mathrm{ate}}}$, as well as octahedral crystals of $\mathrm{Pb\ N}^{\underline{\mathrm{ate}}}$ and cubical crystals of $\mathrm{Ka\ Io}^{\underline{\mathrm{ide}}}$ form thereafter upon spontaneous evaporation. Another good case is that of $\mathrm{Ba\ Cl}^{\underline{\mathrm{ide}}}$ and $\mathrm{H\ S}^{\underline{\mathrm{ate}}}$. Also, $\mathrm{Ca\ S}^{\underline{\mathrm{ate}}}$ and Ammonium Oxalate, and many others. A mixture of $\mathrm{Mg\ S}^{\underline{\mathrm{ate}}}$, $\mathrm{Am\ Cl}^{\underline{\mathrm{ide}}}$, and $\mathrm{Na\ P}^{\underline{\mathrm{ate}}}$, containing enough of $\mathrm{Am\ Cl}^{\underline{\mathrm{ide}}}$ to form a clear solution, gives, with a drop of $\mathrm{Am\ H}^{\underline{\mathrm{ate}}}$, beautiful stellate crystals of hydrous Ammonio-Magnesium Phosphate, often called the "*triple phosphate,*" having the formula $\left.\begin{smallmatrix}\mathrm{Am}\\ \mathrm{Mg}\end{smallmatrix}\right\}\mathrm{O_4\ P} + 6\ \mathrm{H_2O}$.

d. From some crystals it is impossible to obtain an aqueous solution. In this case select the proper solvent. For example, beautiful cubical crystals of silver chloride are obtained by the spontaneous evaporation of a dilute solution of $\mathrm{Ag\ Cl}^{\underline{\mathrm{ide}}}$ in $\mathrm{Am\ H}^{\underline{\mathrm{ate}}}$.†

25. By *cleavage*, corresponding experiments in regard to the minuteness of the atoms may be made. (Phys. 145, 197, 198.) The tabular crystals of $\mathrm{Ka\ Cl}^{\underline{\mathrm{ide}}}$ are well adapted to this purpose — the cleavage, MM′, being obtained by simply pressing a blunt point (say of a pencil) against the largest face, P. It will be seen that even crushed crystals yield a dust, which, under the microscope, exhibits the characteristic form of the crystals themselves, as described in Phys. 179.

---

* The other brilliant colors are due to the thinness of the plates, precisely as the colors of soap bubbles.

† This solution is easily prepared by precipitation of an aqueous solution of $\mathrm{Ag\ N}^{\underline{\mathrm{ate}}}$ by $\mathrm{H\ Cl}^{\underline{\mathrm{ide}}}$, washing the precipitated $\mathrm{Ag\ Cl}^{\underline{\mathrm{ide}}}$ by decantation, and dissolving the same in $\mathrm{Am\ H}^{\underline{\mathrm{ate}}}$.

Among minerals, Calcite and Galenite (Chem. p. 141 and p. 131) constitute the best examples. A fragment of either mineral, crushed by a blow, yields a dust which, under the microscope, exhibits the characteristic cleavage form of the species.

26. These experiments are especially important, because they demonstrate that *the crystal is built up of particles of like form*, throughout. Hence we conclude, *the compound atom possesses a form, closely related to the cleavage form.*

27. As the chemical formulae form the ground-work of theoretical chemistry, it is important that the student should learn how they can be fully verified. (Compare 20.) The following paragraphs explain the methods to be followed in general, and have therefore to be supplemented by *special directions* whenever any experiment is to be performed in the laboratory with any particular compound given to the student by the teacher. A great number of such verifying experiments can most conveniently be made by the use of the so-called *normal solutions*, which are, to a large extent, already in use for volumetric analysis. (See Chem. 208, 150, 180.)

28. *A normal solution of any compound contains one milligram-atom of the compound in each cubic centimeter of the solution.* A milligram-atom represents as many milligrams as the atomic weight contains units. Accordingly, a milligram-atom of oxygen is 16 mgr, and a milligram-atom of carbon 12 mgr.

If the solution contains n milligram-atoms per cubic centimeter, it is called an *n-normal* solution; if it contains $^1/_n$ milligram-atom, it is called an n^{th} *normal* solution. A fifth-normal solution contains, accordingly, $^1/_5$ milligram-atom of the substance in each cubic centimeter.

29. These normal solutions are *prepared* by dissolving the carefully weighed quantity in sufficient water, and diluting until the mark of the flask. (Phys. 10.) Thus, a gram-atom* of any compound will give exactly a litre of normal solution; a decigram-atom will give 100 cc of normal solution; one-fourth gram-atom will furnish a quarter litre of normal solution, etc.

The student should *calculate* the quantities to be taken in a number of cases given by the teacher, and actually *prepare* a hundred cubic centimeters of some of the simpler normal solutions.

30. A given normal solution may frequently be *verified* by weighing the residue which remains upon the evaporation of 5 cc of the same. (Phys. 156.) If possible, the solution should be left to spontaneous evaporation, whereby, in many cases, beautiful crystals will be obtained. Examples: blue vitriol, alum, potassium, bichromate, silver nitrate, lead nitrate. By means of a line of paraffine around the inside margin of the watch-glass, the otherwise troublesome creeping of the crystals will be prevented. The volume of the solution should be taken by means of a pipette; the 5 cc pipette will generally prove the best. (Phys. 13.)

31. The formula of many insoluble compounds can be verified by the *precipitation* of the compound from a normal solution containing either the electro-positive or the electro-negative constituent of the compound. Thus, the formula of silver chloride may be verified by the complete precipitation of any normal solution of $\mathrm{Ag\,N}^{\underline{\mathrm{ate}}}$ by means of $\mathrm{H\,Cl}^{\underline{\mathrm{ide}}}$, and weighing the carefully washed and dried precipitate; or by the precipitation of any normal solution of $\mathrm{H\,Cl}^{\underline{\mathrm{ide}}}$ or $\mathrm{Na\,Cl}^{\underline{\mathrm{ide}}}$ by means of $\mathrm{Ag\,N}^{\underline{\mathrm{ate}}}$. Thus, if 5 cc of fifth-normal $\mathrm{Ag\,N}^{\underline{\mathrm{ate}}}$ solution had been

---

* As many grams as the atomic weight of the substance, or the atomic weight on the scale of H—1 gram.

---

precipitated, the resulting $Ag\,Cl^{\underline{\underline{ide}}}$ must weigh 143.5 mgr, in order that the formula of $Ag\,Cl^{\underline{\underline{ide}}}$ may be $Ag\,Cl$.

In order that the results obtained by the student may be reliable, the laboratory work must be performed *exactly* according to the special directions to be given by the teacher in the laboratory. While some of these directions necessarily vary, according to the substances employed, others are the same for *all* experiments of this kind. To these belong, besides scrupulous care in weighing and measuring: complete precipitation; transfer of the precipitate to the filter without loss; thorough washing and subsequent drying of the precipitate. How to secure these conditions must be shown by the teacher* in the laboratory. Larger manuals on Quantitative Analysis will furnish such directions for those students who have no teacher near them.

32. At times it is advisible to combine a gradual *dissociation* with the precipitation. Thus, a normal solution of $Ca\,Cl^{\underline{\underline{ide}}}$ may first be precipitated by ammonium oxalate, and the precipitated calcium oxalate weighed after careful drying. This oxalate may then be transferred to a platinum crucible, and exposed to a gentle red heat until it is quite white and converted to $Ca\,C^{\underline{\underline{ate}}}$, which is again weighed. Finally, exposing this to the blast-lamp for abont five minutes, it dissociates to $Ca\,O^{\underline{\underline{ide}}}$, which is also weighed. From 5 cc of normal $Ca\,Cl^{\underline{\underline{ide}}}$ should be obtained —

640 mgr $Ca\,O^{\underline{\underline{ate}}}$, if its formula is $Ca\,O_4\,C_2$.
500 " $Ca\,C^{\underline{\underline{ate}}}$, " " " " $Ca\,O_3\,C$.
280 " $Ca\,O^{\underline{\underline{ide}}}$, " " " " $Ca\,O$.

Another very important and instructive example of this kind is the so-called triple phosphate, which may be precipitated from a normal solution of magnesia. Upon drying, at 100° it loses 5 atoms of water, and at a red heat becomes magnesium pyrophosphate. How much of each of these compounds will result from 5 cc of a normal magnesium solution, if the triple phosphate has the formula $Am\,Mg\,O_4\,P + 6\,H_2\,O$, and the pyrophosphate is $Mg_2\,O_7\,P_2$? (See 25, *c.*)

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* If the substance is to be weighed on the filter between the clamp watch-glasses in common use, the teacher should have written the *weight* of the filter on the same before handing it to the student. If the filter is burned, the weight of its ash may be neglected by the student, being only 1 or 2 mgr.

33. It will be found exceedingly convenient and instructive to start with the *metal*, forming a normal solution in sufficient quantity to permit several separate precipitations. Thus the student not only verifies the formula of these several compounds most satisfactorily, but he learns also how these compounds can be obtained. Thus, if 5 milligram-atoms of granulated* lead (*i. e.*, 1035 mgr), are dissolved in pure dilute $H\,N^{\underline{ate}}$ with the aid of a gentle heat, and the solution diluted to 50 cc, we shall have a tenth-normal solution of $Pb\,N^{\underline{ate}}$. By taking 5 cc or 10 cc of this solution, the following formula may be verified:

$Pb\,N^{\underline{ate}}$	is	$Pb(O^3N)_2$	of	atomic	weight	331.
Pb Oxalate	“	$Pb\,O_4\,C_2$	“	“	“	295.
$Pb\,C^{\underline{ate}}$	“	$Pb\,O_3\,C$	“	“	“	267.
$Pb\,S^{\underline{ate}}$	“	$Pb\,O_4\,S$	“	“	“	303.
$Pb\,Cr^{\underline{ate}}$	“	$Pb\,O_4\,Cr$	“	“	“	323.
$Pb\,S^{\underline{ide}}$	“	$Pb\,S$	“	“	“	239.
$Pb\,Io^{\underline{ide}}$	“	$Pb\,Io$	“	“	“	334.

34. In some cases the tedious process of filtration and drying may be avoided. Thus, the $Pb\,S^{\underline{ate}}$ may be obtained by adding $H\,S^{\underline{ate}}$ to the solution of $Pb\,N^{\underline{ate}}$ and very carefully evaporating to dryness in a porcelain dish on a sand-bath, and heating as long as white fumes of the slight excess of $H\,S^{\underline{ate}}$ continue to pass off. (Compare Chem. 195 and 188.

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* Obtained by pouring melted lead into cold water which is constantly stirred.

The same may be done with a weighed off quantity of $\mathrm{Na\,Cl}^{\underline{\underline{\mathrm{ide}}}}$ or $\mathrm{Ka\,N}^{\underline{\underline{\mathrm{ate}}}}$, etc.; the weight of the sulphate will verify the formula $\mathrm{Na_2\,O_4\,S}$ and $\mathrm{Ka_2\,O_4\,S}$. In these experiments double decomposition takes place, on account of the greater volatility of the $\mathrm{H\,Cl}^{\underline{\underline{\mathrm{ide}}}}$ and $\mathrm{H\,N}^{\underline{\underline{\mathrm{ate}}}}$, and the excess of the less volatile $\mathrm{H\,S}^{\underline{\underline{\mathrm{ate}}}}$ is destroyed by dissociation, so as to leave the non-volatile metallic sulphate in a pure state.

35. The all-important formula of water, $\mathrm{H_2\,O}$, is best verified by collecting and weighing the water formed when hydrogen gas passes over heated cupric oxide (see Chem. 176). Let the weight of the cupric oxide taken be a, the weight of the copper remaining be b, and the weight of the water formed and *collected* (see Chem. 157) be c. Then the weight of oxygen in this water will be $a-b$. The most accurate experiments show that $a-b$ is to c as 8 is to 9, exactly; or, that in every 9 milligrams of water there are 8 milligrams of oxygen, and consequently 1 milligram of hydrogen.

By the combustion of pure carbon the formula, $\mathrm{C\,O_2}$, of carbon dioxide has been verified, as indicated. (Chem. 155.)

Show how the values stated in Chem. 155 and 158 verify these formulae.

36. The innumerable quantitative analyses constantly being made by investigators in all parts of the world, really constitute most important confirmations of the generally accepted chemical formulæ which have been given in the preceding articles, as based upon the atomic weights of article 18. Every new compound thus far obtained — and in modern days new compounds are formed by the hundred every year — has confirmed these atomic weights in the same manner.

37. The grand general result of the quantitative chemical experiments sketched in the preceding articles, and of the most accurate quantitative researches of modern chemists, may accordingly be stated in the following manner:

The quantitative composition of all chemical compounds can be expressed by chemical formulæ, wherein the symbols represent the atomic weights (tabulated in article 18) *of the elements, each atomic weight repeated but a few and whole number of times* (such as 1, 2, 3, 4, etc., times).

The above is simply a general statement of the *facts*—involving no theory in regard to the existence of atoms whatever.

38. The above fundamental law of theoretical chemistry may also be expressed as follows:

The chemical elements combine with one another in fixed, simple, and multiple proportions—a simple (low) and whole number of times the atomic weight of article 18 being contained in the atomic weight of any compound.

Here, again, the term "*atomic weight*" means simply that number of any units of weight given in article 18. Accordingly, this law is strictly empirical, and often spoken of as "*the law of simple multiple proportions.*"

39. It will, however, be perceived that this empirical law is a simple consequence of the reality of atoms. For if matter consists of atoms, then the elements can only form new compound-atoms by the combination of a *whole number* of atoms of the different combining elements; and this number will, for the more simple compounds, be rather small—such as 1, 2, 3, 4, etc.

Therefore, *the empirical law of multiple proportions* (37 and 38) *indicates the* REALITY OF ATOMS (13). If the atoms were not real, it would be impossible to comprehend why the elements do combine in fixed proportions, which are simple multiples of certain fixed weights, peculiar to each element.

40. The quantitative chemical experiments here made use of are not sufficient to fix the precise value of the atomic weights themselves, but can determine only a *multiple* or *sub-multiple* of the same; for the quantitative experiments determine only *ratios* of weight, and not absolute weights.

Thus, $H = 1$ being the standard (see 17), the quantitative analysis of water gives the atomic weight of oxygen as $O = 16$ if the formula of water be H_2O, but as $O = 8$ if the formula of water be HO; for the analysis of water (35) simply determines the *ratio* of the weight of hydrogen to that of oxygen in water is as *one* to *eight.* In other words, if we assume that each atom of water contains but *one* atom of hydrogen, then $O = 8$ if each atom of water contains but one atom of oxygen also, or is HO. If, however, we suppose that each atom of water contains *two* atoms of hydrogen and but one of oxygen — that is, if the formula of water is H_2O — the atomic weight of oxygen is determined by the proportion $H_2 : O = 1 : 8$ given by the analysis as $O = 16$. (Compare Chem. 102.)

This uncertainty in regard to the absolute value of the atomic weights cannot be removed by quantitative *chemical* experiments — it is removed by the *physical* experiments on expansion of gases and specific heat now to be studied.

Section II. Chemical Molecules.

41. *A chemical molecule is a group of atoms moving as one solid body* — that is, the atoms which constitute a molecule retain the same relative position, although they all may move in any direction.

If we take beads of different color and weight to represent the atoms of different elements, and attach a number of such beads, by means of rigid metallic wires, to one another, so as to form a rigid system of mutually distant beads, this system may properly represent a chemical molecule.

42. The weight of the molecule is the sum of the weight of all the atoms constituting the same; it is usually termed the *molecular weight*[*] of the substance (element or compound). The molecular weight of hydrogen is about 0.005 micrograms. (Compare 22.)

The volume occupied by one molecule is the *molecular volume* of the substance.

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[*] **42, *a*.** The absolute weight of the atoms being not accurately known, it follows that the absolute molecular volume and weight also is not yet accurately known. (Compare 21, 22, 23.)

At 0° C and under a pressure of 760 mm, *one molecule* of hydrogen occupies about fifty cubic millimicrons (50 cub. $m\mu$), according to Maxwell. In other words, one cubic millimeter of hydrogen gas contains about 20,000,000,000,000,000 molecules. Each molecule of hydrogen gas consists, furthermore, of two atoms of hydrogen.

42, *b*. In practice, we use the *milligram-molecule*—that is, an amount of the substance weighing as many milligrams as the molecular weight of the substance has units. Similarily the gram-molecule, etc., exactly as in the case of the atomic weights. (See 28.)

42, *c*. According to the modern mechanical theory of heat, all molecules are in constant and very rapid vibratory motion. (See Chem. 80, 90.) The absolute temperature, T, of a body is proportional to the *vis viva* or actual energy of the molecules of the body; that is, the absolute temperature, T, of that body is *proportional* to the product $w. v^2$ of the molecular weight w into the square of the velocity v of the molecules. (Compare Induct. 59.)

42, *d*. The *absolute temperature*, T, is equal to 273 *plus* the centigrade temperaperature, t, of any body; that is, $T = 273° + t°$ C. (Compare Induct. 37.) Thus, the absolute temperatures of the freezing and boiling points of water are 273° and 373°.

42, *e*. The velocity of the molecules of hydrogen gas at the freezing point (0° C) is 1,860 meters per second. Oxygen molecules move at the same temperature with a velocity of only 465 meters. In fact, the greater the molecular weight, the smaller must (by *c*) be the molecular velocity at the same temperature.

42, *f*. The molecules of these gases do not continue their motion undisturbed very long; they strike against neighboring molecules or the walls of the containing vessel, and rebound therefrom. Thus, the molecules of hydrogen gas continue their path, on the average, only 96 millimicrons, while oxygen molecules have a mean path of only 56 millimicrons; for the hydrogen molecules collide against each other 17,750,000,000 times a second, and oxygen molecules 7,646,000,000 times a second.

42, *g*. The *pressure* of gases on the walls of the containing vessel is due to the continuous impact of the minute molecules against the walls. The ponderous piston is pushed along the cylinder simply by the impact of the excessively minute molecules of steam which in excessively great numbers impinge, at incredibly short intervals of time, against the piston with a velocity of several hundred meters.

42, *h*. The preceding statcments are simply borrowed from the mechanical theory of heat. A proper combination of these laws has led to the following result, which is of the utmost importance to theoretical chemistry:

The molecular volume of all gaseous substances is equal— at the same temperature, and under the same pressure.

This law, here indicated as a direct consequence of the mechanical theory of heat, is used in the text simply as an *empirical law*, or even as a physical hypothesis.

43. The following hypothesis — itself a consequence of the mechanical theory of heat — was first proposed in 1811, by *Avogadro*, as the relation between atom and molecule in the gaseous condition:

The molecule of gaseous elements consists of two atoms; the molecule of gaseous compounds consists of one atom of the compound.

Accordingly, the molecular weight of hydrogen is $H_2 = 2$; of oxygen, $O_2 = 32$; of chlorine, $Cl_2 = 71$, etc. (See 18.) The molecular weight of water, H_2O, will be 18; of ammonia, H_3N, it will be 17; of hydrogen chloride, HCl, it will be 36.5; of marsh gas, H_4C, it is 16, according to the formula.

44. *The molecular volume, v, of all gaseous substances is equal*, for the same temperature, t, and pressure, p — that is, *the volume of a milligram-molecule of any gaseous substance is equal to the volume occupied by two milligrams of hydrogen gas* under the same pressure and at the same temperature.

This law is also a simple consequence of the mechanical theory of heat, and may be readily demonstrated to be a *fact* by experiment. At 20° C and under 760 mm pressure, 2 mgr hydrogen occupy exactly 24 cubic centimeters. An equal volume will, under the same circumstances, hold 32 mgr oxygen gas, 71 mgr chlorine, 28 mgr nitrogen, 16 mgr marsh gas, 36.5 mgr hydrogen chloride, 28 mgr carbon oxide, 44 mgr carbon dioxide, etc., etc. Since now equal volumes of all gases remain equal under equal changes of temperature and pressure,* these milligram-molecular volumes will remain equal so long as the pressure and temperature remain the same for all. Experimentally, this may be shown by *Hofmann's* apparatus,† which consists of four glass tubes, containing equal volumes of four different gases over mercury, which stands to the same level in the four tubes, and communicates with a reservoir of mercury. If now the level of the mercury in this reservoir is raised or lowered, the pressure will be *equally* increased or diminished for the four gases — but their volume will remain mutually equal. These volumes will also remain equal, if the four tubes are equally heated or cooled. (Compare Induct. 37.)

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* The so-called *Gay-Lussac-Mariotte's Law*. (Induct. 37.)

† Introduction to Modern Chemistry.

45. The combination of the laws (43 and 44) leads to a general law regulating the relation of the *sum* of the volumes of the uncombined constituents and the volume of the resulting compound, viz:

Whatever the sum of the volumes of the uncombined gaseous elements, the compound atom resulting by this combination is always of equal volume — and equal to the molecular volume of hydrogen. That is, if any two gaseous elements, A and B, combine,—

1 vol. A + 1 vol. B, *i. e.* 2 vols. of the mixture, give 2 vols. of the compound AB;

2 vols. A + 1 vol. B, *i. e.* 3 vols. of the mixture, give 2 vols. of the compound A_2B;

3 vols. A + 1 vol. B, *i. e.* 4 vols. of the mixture, give 2 vols. of the compound A_3B;

3 vols. A + 2 vols. B, *i. e.* 5 vols. of the mixture, give 2 vols. of the compound A_3B_2;

4 vols. A + 2 vols. B, *i. e.* 6 vols. of the mixture, give 2 vols. of the compound A_4B_2;

5 vols. A + 1 vol. B, *i. e.* 6 vols. of the mixture, give 2 vols. of the compound A_5B;

etc., etc., etc.

This is equally true for ternaries and higher compounds. Thus,—

1 vol. A + 1 vol. B + 1 vol. C, *i. e.* 3 vols. mixture, give 2 vols. of the compound ABC;

1 vol. A + 2 vols. B + 1 vol. C, *i. e.* 4 vols. mixture, give 2 vols. of the compound AB_2C;

etc., etc.

This law has, at first sight, the appearance of a paradox, and may be termed the *chemical paradox*, but it is evidently but another instance of the general *difference* between compound and mixture. (See Chem. 97.)

46. Since the molecule of gaseous elements consists of two atoms (see 43), and since the molecular volume of all gaseous substances is equal (see 44), it follows, from the very nature of the atom (see 39), that *gaseous elements combine only in simple multiple proportions by volume*, such as 1 and 1, 1 and 2, 1 and 3, 2 and 3, etc., etc. (Compare 45.) This was first discovered by *Gay-Lussac.* The most striking confirmation hereof, we have in the electrolysis of compounds which yield *two* gaseous elements. Thus, the electrolysis of water gives gaseous oxygen and hydrogen *exactly* in the proportion of 1 : 2 by volume. So, also, hydrogen chloride gives the hydrogen and the chlorine exactly in the proportion of one to one by volume. In like manner, ammonia yields one volume of nitrogen for every three volumes of hydrogen, exactly. (See Hofmann's Introduction to Modern Chemistry for experimental and other details on this subject.)

47. It is evident that this electrolysis immediately establishes the formula of the compound; for, taking the one (smaller) volume as unit, as representing one atom, the other volume will represent 1, 2, 3, etc., atoms (44). Accordingly, the electrolysis of hydrogen chloride shows this compound to possess the formula $H\,Cl$; water, H_2O; ammonia, H_3N; etc.

48. The chemical paradox (45) enables us also to determine the chemical formula of a gaseous compound, if it, by *dissociotion*, gives at least one gaseous element. Thus, marsh gas gives, upon dissociation, by a series of electric sparks, a volume of hydrogen *twice* as great; accordingly, one molecule of marsh gas contains two molecules, or four atoms, of hydrogen. The carbon deposited by dissociation being taken as *one* atom, the formula of marsh gas will be H_4C.

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49. The same application of the chemical paradox may be made if a *synthesis* is readily effected. Thus, a fragment of carbon will burn in pure oxygen, yielding a volume of carbon dioxide exactly equal to the oxygen taken. Hence, one molecule of carbon dioxide contains one molecule of oxygen, that is, *two* atoms of oxygen; consequently, the formula of carbon dioxide is CO_2.

50. The harmony of the results thus obtained by Avogadro's law (44 and 43) in all possible combinations, is the best confirmation of the law. Thus, the molecular weight of marsh gas being, according to experiment, 16, the atomic weight of carbon must be $C = 12$. (See 48.) The same value, $C = 12$, follows from 49, since experiment has given the molecular weight of carbon dioxide gas as 44.

51. The application of the law (44) necessitates the knowledge of the molecular volume of gaseous substances for any given temperature, t° C, or pressure, p mm. By the observation of the volume, v, cubic centimeter of one milligram-molecule of hydrogen gas (*i. e.* 2 mgr) under different pressures and temperatures, the volume of a milligram-molecule would evidently become accurately known. By accurate experiments of this kind, it has been ascertained that the two milligrams of hydrogen occupy, at 20° C and under 760 mm pressure, a volume of 24 cc; at 48° and under 1000 mm pressure, a volume of 20 cc; etc.

52. In general, the volume of one milligram-molecule of any gas is equal to —

$$v = \frac{20,000 + 73.4\,\tau}{p} \text{ cubic centimeters,*}$$

wherein $\tau = t - 48°$ centigrade.

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* This is the simplest form of the Gay-Lussac-Mariotte's law for calculation purposes. At 48° and under 1,000 mm pressure, the volume is 20 cc (see 51); hence, by Mariotte's or Boyle's law, it will be —

$$v = 20\,\frac{1,000}{p} = \frac{20,000}{p}$$

For example: at 65° C and under 530 mm, the volume of a milligram-molecule is 40.09 cc; for here $\tau = 65 - 48 = 17$, consequently 73 4 τ will be 1247.8, and 21247.8 divided by 530 gives 40.09.

53. Consequently, if, under any convenient pressure, p, and at any temperature, t, we observe the volume, V cc, of a known weight, W mgr, of any gas, we can calculate the molecular weight, w, of that gas. For, by 52 we obtain the molecular volume, v cc, under these circumstances; hence in the total volume, V, there are —

$$n = \frac{V}{v}$$

milligram-molecules, each of which, therefore, must weigh —

$$w = \frac{W}{n} = \frac{W}{V} \cdot v$$

milligrams.

54. If the gas is a compound, then this value, w, will be the atomic weight of that gas. If, however, the gas be an element, its atomic weight will be one-half of this value. (Compare 43.)

By this method, the molecular and atomic weights of all gaseous bodies can therefore be determined. The same method is also largely applicable to vapors.

55. For *permanent gases*, W is obtained as the difference between the weight of a large glass balloon when filled with the dry, pure gas (at t and under p observed) and when completely exhausted (by means of a mercury pump); V is thereafter ascertained from the weight of the ballon filled with water.

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at the pressure of p mm, and according to Gay-Lussac's law it will be —

$$v = \frac{20,000}{p} (1 + 0.00367\ \tau)$$

at τ degrees from 48°. This is the above expression. (Compare Induct. 37).

In this manner Regnault has determined the atomic weight of hydrogen, oxygen, nitrogen, and other gases.

56. For the purpose of verification by the student, we make use of the following method, here exemplified by carbon dioxide:

Take a fragment of calcite (or marble) weighing three to four decigrams; let its weight be a mgr — then we know, from Chem. 141 or 190, that it contains W = 0.44 a of carbon dioxide. By means of our gas-burette, the volume, V, of carbon dioxide contained herein is next determined, while temperature and pressure is noted. Thus, all data necessary for the determination of the molecular weight have been obtained.

57. For very volatile vapors, Hofmann's modification of Gay-Lussac's method is most convenient. In a minute, completely filled, glass stoppered vial, the weight, W, of the liquid is determined. This filled vial is then slipped into a wide torricellian tube (Phys. 130); as it reaches the vacuum, the stopper flies off, the liquid volatilizes, and its vapor depresses the mercury column. By surrounding the tube with a wider one, through which a current of steam passes, the complete volatilization is readily secured, even if the liquid be less volatile than water. The temperature is read off on a thermometer in this current of steam. The pressure under which this vapor stands is equal to the difference between the barometer and the height of the mercury in this torricellian tube. Finally the volume, V, filled by the vapor is directly read off on the same tube. Thus, all quantities necessary for the determination of the molecular (or atomic) weight have been determined. (See 53, 54.)

58. If the substance be less readily volatile, Dumas' method is used for the determination of the molecular weight. A glass balloon of thin glass, having a long and narrow neck drawn out to a fine tube, is weighed when filled with air and when filled with vapor under a known pressure, p, and at a known temperature, t; thereby W is determined. Breaking off the point of the tube under mercury, the latter will fill the balloon; weighing with mercury will give the capacity of the balloon, that is, the volume, V, of the vapor. Hence, again, all quantities necessary have been determined.

To fill the balloon with the vapor, it is gently heated, then its point is immersed in the liquid; as the balloon cools, enough of the liquid will ascend to serve for the determination. The balloon is then fastened in a water or oil bath (Chem. 19), and gradually heated; when the vapor ceases to issue from the narrow neck, this is sealed by means of the blow-pipe flame, while at the same time the barometer and thermometer are read off.

59. If the balloon be of porcelain, and the bath an oven filled with the vapor of some boiling metal,* the molecular weight of less volatile substances can be determined. In this manner, the vapor densities of ferric chloride, aluminium chloride, etc., have been determined by Deville.

60. By this method, the molecular weight of volatile substances may also be determined at very high temperatures in order to ascertain whether the molecular weight remains the same, or not. In the latter case, evidently a *dissociation* takes place. (Chem. 93.)

61. Thus, the molecular weight of sulphur had been found to be 192 at moderately high temperatures (about 400° to 500° C). Consequently, one molecule of sulphur vapor at these temperatures is S_6, containing six atoms of sulphur, $S = 32$, and not two, as required by Avogadro's law. Hence, by many chemists this law was for a long time discarded; but Deville found that the molecular weight of sulphur vapor is 64 at high temperatures (see 59); hence the formula of its molecule is $S_2 = 64$, as required by the law of Avogadro.

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* The baths more commonly used are: boiling mercury, 350°; cadmium, 860°; zinc, 1040°. Sulphur, boiling at 440°, is also used.

62. In a like manner phosporus and arsenic deviate from the law, their observed molecular formulæ being P_4 and As_4, and not P_2 and As_2, as the law requires. Evidently, here a like higher *molecular combination* of these elements has so far been observed as vapor.

63. These facts have a high importance in regard to the so-called *allotropic conditions* of certain elements. Thus, sulphur changes to a viscid allotropic condition when heated between 150° and 250°. Phosphorus changes to the red, non-poisonous variety when heated under pressure at 240°, in an atmosphere of hydrogen or carbon dioxide. Oxygen changes to the more active *ozone* when properly electrified; and the molecular weight of ozone is $48 = O_3$, while that of oxygen is $32 = O_2$.

The *diamond* is probably a higher molecular combination of carbon than common carbon. This is confirmed by the low specific heat of the diamond, as will appear in a subsequent section. (See 77.)

64. In a like manner, many apparent exceptions exhibited by compounds have formerly been considered as weighty objections to the adoption of Avogadro's law; but now it is known that these exceptions are due to the more or less complete *dissociation* of the vapors. Thus, sal-ammoniac, or ammonium chloride, Am Cl, is $NH_4Cl = 53.5$, since it readily forms as white cloud when ammonia, NH_3, and hydrogen chloride, HCl, vapors meet. Yet the molecular weight of sal-ammoniac was found to be only 26.75, or one-half of its atomic weight, 53.5. But it is now known that this salt can only exist undecomposed below 90°, and is *completely* dissociated at 340° C; hence, at this temperature, or above the same, we have *not* the vapor of sal-ammonia at all, but a mixture of equal volumes of H Cl, the molecular weight of which is 36.5, and of NH_3, the molecular weight of which is 17; hence the apparent molecular weight observed is the mean of these two values — *i. e.*, 26.75, or one-half of 53.5.

The same is evidently the case for mercury and cadmium; their vapor, thus far known, is atomically dissociated.

65. Very far from invalidating the law of Avogadro (44 and 45), the apparent exceptions to the same, whether offered by elements or compounds, have, so far, constantly contributed to furnish new, unlooked-for, and very decisive confirmations of the same. In fact, this law has largely become the basis of modern theoretical chemistry.

66. Unfortunately this law is, by its very nature, restricted to gaseous substances, or, at most, to vapors which are considerably heated above the boiling point of their liquid. It is true that the law enables us to determine the atomic weight of even fixed substances with a high degree of *probability.* (Compare 48 and 49, where $C = 12$ has been found.) But the aid of some additional physical law, which may embrace both volatile and non-volatile elements, is required, in order that the atomic weight of the metals may become known with perfect certainty.

Such a law was discovered in 1819, in regard to the specific heat of the elements, as explained in the next section.

Section III. Atomic Heat.

67. *The specific heat of the elementary atoms is nearly the same for all elements.* (Dulong and Petit's Law, 1819.)

The specific heat of an atom is, of course, the number of calories required to heat one atom one degree centigrade. (Chem. 48.)

68. The *absolute* weight of the atoms being not accurately known, it is necessary here again to make use of the *relative* atomic weights. The unit H = one gram, *i. e.* the *gram-atoms,* will be most convenient.

Accordingly, the law of Dulong and Petit may be expressed as follows:

The specific heat of the gram-atom of any element is nearly 6.3 *calories.*

In other words, to raise the temperature of one gram-atom of any element one degree, requires nearly as much heat as to raise the temperature of 6.3 grams of water one degree.

69. If $\underline{a}$ represents the atomic weight, and $\underline{s}$ the specific heat, the product $\underline{a.s}$ will be the specific heat $\underline{S}$ of a gram-atom of the substance. (Chem. 49.) Consequently, 68 may be expressed by the formula—

$$S = a.s \text{ nearly equal to } \underline{6.3}.$$

70. Conversely, if the specific heat, s, of an element be known, 70 will give an approximate determination of the atomic weight of the same element, namely:

$$\underline{a} \text{ nearly } \frac{6.3}{s}$$

Thus, to raise the temperature of one gram of lead one degree requires 0.031 calories. (Chem. 52.) Consequently, the atomic weight of lead must be about 6.3 divided by 0.031, or 200; the true and exact value, Pb, is 207. (See 18.)

71. It is apparent that this law, although it not at all determines the atomic weight of any element with *numerical* precision, furnishes exactly that guide which was lacking (see 38 to 40), but essential. Thus, the quantitative analysis of yellow lead oxide shows that O = 16 of oxygen are united with 207 of lead. But this number, 207, may be 1, 2, 3, etc., atoms of lead, or even $^1/_2$, $^1/_3$, etc., atoms of lead, if the formula of lead oxide is respectively $Pb\,O$, $Pb_2\,O$, $Pb_3\,O$, etc., or even $Pb\,O_2$, $Pb\,O_3$, etc. Since lead oxide is not volatile enough to admit of the determination of its molecular weight in the gaseous condition, we see that we need some criterion whereby to determine which of the numbers —

207.........103.5......... 69, etc.,
207.........414 ....621, etc.,

is the atomic weight of lead. And we see that the above result from the law of Dulong and Petit is perfectly sufficient; for, of all these values, only 207 is near 200. Hence the atomic weight of lead is $Pb = 207$, and the formula of the yellow lead oxide is $Pb\,O$.

In a like manner, the atomic weight of the other non-volatile elements is determined by a combination of the results of analysis with this law.

72. The following table gives the specific heat of the principal elements in alphabetical order of the symbols. They have been obtained by different experimentors, especially by Regnault, by methods based upon the principles explained. (Chem. 48 to 52.) It will be remembered that these figures express the number of calories (Chem. 43) required to raise the temperature of *one gram* of any of these elements one degree centigrade.

Ag	0.057	Cl	....	Li	0.94	Rh	0.058
Al	0.214	Co	0.108	Mg	0.25	S	0.203
As	0.081	Cr	....	Mn	0.122	Sb	0.051
Au	0.032	Cu	0.095	N	....	Se	0.076
Ba	....	Fe	0.114	Na	0.293	Si	0.177
Bi	0.031	Fl	....	Ni	0.108	Sn	0.056
Bo	0.250	H	....	O	....	Sr	....
Br	0.084	Hg	0.033	P	0.189	Te	0.052
C	0.147	Ir	0.033	Pb	0.031	Ti	....
Ca	....	Io	0.054	Pd	0.059	Ur	....
Cd	0.057	Ka	0.170	Pt	0.032	Zn	0.096

The values here given are for —

Bo, crystallized; when amorphous, 0.235.
Br, solid.
C, as diamond; graphite gives 0.205.
Hg, liquid; when solid, 0.025.

73. *The specific heat of the gram-atoms of the elements* have, therefore (69), the numerical values represented in the following systematic table of the elements (Chem. 111). The numeral values of s are taken from 72, and those of a from 18.

	MEAN.*	I.	II.	III.	IV.	V.
Ka	....	Li 6.6	Na 6.8	Ka 6.6	....	....
Xa	....	....	....	Ca	Sr	Ba ....
Kδ	6.3	....	Mg 6.0	Zn 6.3	Cd 6.4	Pb 6.4
Γγ	....	....	....	....	....	Hg 6.6
Kν	6.2	....	....	Cu 6.0	Ag 6.2	Au 6.3
Σι	6.3	....	Al 5.9	Fe 6.4	Rh 6.0	Ir 6.5
Tτ	6.3	C 2.8	Si 5.0	Ti	Pd 6.3	Pt 6.3
....	....	Bo 2.8	....	....	Sn 6.6	....
Φ	6.3	N	P 5.9	As 6.1	Sb 6.2	Bi 6.5
Θ	6.3	O	S 6.5	Se 6.0	Te 6.6	....
X	6.7	Fl	Cl	Br 6.7	Io 6.8	....
Mean of vertical columns			6.0	6.3	6.4	6.5
Σδ		Cr....	Mn 6.7	Fe 6.4	Ni 6.3	Co 6.5

The mean of all values in the II., III., IV., V. columns is 6.33, or $6^1/_3$ calories.

74. From this table, it is evident that the specific heat of the atoms of different (solid) elements, is nearly equal to 6.3, thus confirming the law of Dulong and Petit (68). Inversely, therefore, the specific heats observed and tabulated in 72 prove the correctness of the atomic weights adopted, even for solid elements. (See 66.)

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* Mean of the values in columns headed III., IV., V., only.

75. For several elements, we have both the determination of the atomic weight from the molecular weight of the vapor and from the specific heat, and the two altogether independent determinations agree. This is the case for S, Br, Io, and some others.

76. Accordingly, the atomic weights of the elements adopted (see 18), are not only *exact* in the precise amonnt, as determined by accurate quantitative analyses, but also atomically *correct*, being neither a multiple nor a sub-multiple of the true atomic weights. (Compare 40.)

77. The case of carbon, as diamond, seems exceptional — the atomic specific heat being only 2.8, instead of 6.3. But the diamond is probably a molecular combination of carbon (see 63), perhaps consisting of molecules of two atoms each, which double-carbon atoms are comparable to the atoms of other elements. In that case the specific heat of the diamond-atom would be 5.6, and thus be nearly normal, since the means of the vertical columns of the table (73) show that the atomic specific heat generally increases with the atomic weight of the element in the same genus. Herewith agrees the fact that the specific heat of graphite is 0.205, or 1.4 times that of the diamond, while charcoal has a specific heat of 0.242, or even 1.6 times that of the diamond — hence approaching to a condition of carbon of single atoms. The other physical properties of the diamond also indicates that it is a double-atom form of carbon. Of course, by combustion, these atom-groups will dissociate, giving the same product of combustion* as any other variety of carbon.

78. In molecular mechanics it is shown that the specific heat of the atoms in the solid condition of the elements is a very complex quantity, involving especially the so-called "*internal work.*" Hence we cannot expect any closer agreement of the atomic specific heat than exhibited in the above table (78). (Compare Chem. 80; and, in general, the second chapter of the Elements of Chemistry.)

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* But a less heat of combustion!

79. For gases and vapors, Regnault has determined the specific heat, s′, for the unit of volume of atmospheric air at 0° and 760 mm. Hence, the specific heat, S′, of a *molecule* of any gas can be calculated by —

$$S' = 28.94\, s',$$

since it takes 28.94 cc of hydrogen under 0° and 760 mm to weigh as much as 2 cc of atmospheric air. It follows, further, that the specific heat of an *atom* of a gaseous element will be $\frac{1}{2}$ S′. (See 43.)

80. The following table contains the values of s′ determined by Regnault's experiments on the elementary gases, together with the specific heat of the *atom* (S) and the molecule (S′) of the same gases, calculated by 79:

NAME.	s	ATOM.		S	MOLECULE.		S′
Hydrogen	0.236	H	1	3.41	H_2	2	6.83
Nitrogen	0.237	N	14	3.43	N_2	28	6.86
Oxygen	0.241	O	16	3.48	O_2	32	6.97
Chlorine	0.296	Cl	35.5	3.78	Cl_2	71	8.57
Bromine	0.307	Br	80	4.44	Br_2	160	8.88

81. From the values of the atomic specific heat, S, of these gases and vapors, we see that it is *much smaller* than for the solid elements. The mean of the permament gases H, N, O, is 3.44, against 6.33, found for the metals (74). This is in perfect harmony with the well known fact of molecular mechanics, that the internal work in gases is much less than in solids. According to the above it is 6.33 — 3.44, or 2.89 calories *less* for every gram-atom in the gaseous condition, as compared to the same atom as part of a solid element. (Compare 78.)

82. If the internal work in elementary gases were zero, then 2.9 of the 6.3 calories required to raise the temperature of one gram-atom one degree centigrade would be consumed to accomplish internal work. In other words, 46 per cent of the heat consumed would, in solid elements, do internal work — *i. e.*, overcome the attraction of the molecules, etc.

This shows how impossible it is that the values of 73 should be exactly equal, for the internal work is certainly not equal in the different elements.

83. It will be noticed that the specific atom-heat (4.4) of bromine vapor is much greater than that of the permanent gases (3.4), but much smaller than that of liquid bromine (6.7). This also agrees with the molecular condition of these forms of matter. In one atom of bromine-vapor, the internal work consumes 1.0 calories, while in one atom of liquid bromine 4.3 calories appear to be consumed in the internal work done by lifting the atoms farther apart, etc.

84. In compound atoms, the component atoms retain nearly the same specific heat they have in the free state, so that the *specific heat*, S′, *of a compound atom is nearly equal to the sum*, S, *of the specific heat of the several atoms of which it is formed.* But the internal work, varying, will produce greater or less differences, d, between this sum and the observed atomic heat of the compound.

85. For a few compound gases and vapors, we take the observed values, s, from Regnault's determinations:

NAME.	FORMULA.	a	s′	S′	S	d
Water	H_2O	18	0.299	8.653	10.30	—1.65
H Cl$^{\underline{ide}}$	HCl	36.5	0.233	6.743	7.19	—0.45
Nitrous Oxide	N_2O	44	0.345	9.985	10.34	—0.35
Ammonia	H_3N	17	0.300	8.683	13.66	—4.98

These differences are all negative, S greater than S′, and of various magnitudes — thus very plainly disprove the assertion of Kopp, that the specific heat of the atoms remains the same in its compounds, and proves that these specific heats comprise often a large quantity of internal molecular work.

86. Accordingly, we cannot expect that the specific heat of a compound atom is *equal* to the sum of the specific heat of the constituent atoms, except so far as the internal work is nearly the same in the compound and in its components.

This is confirmed by the following table, giving the name, formula, atomic weight (a), specific heat (s), specific heat of the atom ($S = a . s$) (see 69) of several compounds, and also (from 73) the *sum* (S′) of the specific heat of the constituent atoms, together with the difference (d) between S and S′.

NAME.	FORMULA.	a	s	S	S′	d
Lead bromide	$PbBr_2$	367	0.053	19.6	19.8	0.2
“ rodide	$PbIo_2$	461	0.043	19.7	20.0	0.3
Mercuric chlor.	$HgCl_2$	271	0.069	18.7	20.0	1.3
“ iodide	$HgIo_2$	454	0.042	19.1	20.2	1.1
Galenite	PbS	239	0.051	12.2	12.9	0.5
Sphalerite	ZnS	97.2	0·115	11.2	12.8	1.6

In these cases, the differences, d, expressive of the differences of internal work, are of very different magnitude, as was expected.

87. In looking back upon the results in regard to the specific heat, we recognize in the empirical law of Dulong and Petit a most valuable means for the determination of an approximate value of the atomic weight of solid elements (see 70), giving results in accordance with those obtained by the law of Avogadro (75 and 76).

88. Above all, it ought to be recognized that the *values* assigned to the atomic weights of the elements in 18 are correct, representing the quantitative composition of all known compounds, and satisfying the requirements of two entirely different physical laws, namely: the law of Avogadro (43, 44), and the law of Dulong and Petit (67, 68).

89. In the following portions of this work, we shall therefore constantly employ these values of the atomic weights of the elements, and treat the chemical atoms as realities. We shall find that the consequences deduced are most completely confirmed by experience, thus adding new and very important confirmations of the reality of chemical atoms to those thus far adduced.

90. The results of the atomic theory in regard to atomicity, substitution, isomerism, and isomorphism, are of special importance in regard to the reality of the chemical atom as here defined (see 13). These topics will now be treated of.

Section IV. Atomicity, or Valence.

91. Comparing the most common hydrogen-compounds, the formula of which is established by electrolysis (47) or dissociation (48), we notice that *one atom of a given element combines with a certain, fixed number of hydrogen atoms only.* Thus, one atom of *chlorine* combines with *one* atom of hydrogen to form hydrogen chloride, HCl; one atom of *oxygen* with two atoms of hydrogen to one atom of water, H_2O; one atom of *nitrogen* combines with *three* atoms of hydrogen to form ammonia; H_3N; and, finally, one atom of *carbon* combines with *four* atoms of hydrogen to one atom of marsh gas, H_4C. One atom of either of these elements does never take up more than the number of hydrogen atoms here stated.

92. Again, carbon dioxide, CO_2, is completely saturated with oxygen — any amount of oxygen in excess of two atoms for each one carbon atom has, under all circumstances, remained in the free, uncombined state. Now, it is evident that there is a close relation between the formulæ H_2O, CO_2, and H_4C; for H_2O is saturated

— that is, one atom of oxygen saturates two atoms of hydrogen. Hence, the two atoms of oxygen in CO_2 would saturate four atoms of hydrogen, precisely the number of hydrogen in marsh gas, CH_4; or, we may say, CO_2 is CH_4, wherein $H_4 = 2\ H_2$ is *replaced by* $2\ O$.

93. From the great multitude of kindred facts, the following definition of *valence*, or *atomicity*, has been deduced:

The number of hydrogen atoms required to either saturate or replace one atom of any element, is called the valence of that element.

Thus, the valence, or value, of hydrogen is taken as *unity*, precisely as its atomic weight — simply because its atomic weight is the smallest. The valence of chlorine is *one;* of oxygen, *two;* of nitrogen, *three;* and of carbon, *four* — according to the above formulæ. Why?

Some chemists employ the terms, *atomicity*, *quantivalence*, *bonds*, *affinities*, in the same sense as we use valence.

The compounds HCl, H_2O, H_3N, H_4C, upon which this doctrine of valence finally rests, are called *typical compounds.*

94. The elements having an atomicity of *one* are *monatomic*, or *univalent*, elements. Those the atomicity of which is two are said to be *diatomic*, or *bivalent*. *Triatomic*, or *trivalent*, elements have an atomicity of three. Elements the atomicity of which is four are named *tetratomic*, or *quadrivalent.*

Some chemists recognize atomicities of five and six, but we consider four as the highest valence warranted by facts.

95. The elements having an odd number of atomicities are, by some authors, spoken of as *perissads.* By *artiads* they then mean those elements the atomicity of which is an even number. Thus, H, and Cl, and N are perissads; O and C are artiads.

However, we fail to see the importance of this distinction, upon which some chemists have tried to construct a classification of the elements.

96. To determine the valence of any element, we must know its saturated compounds with any of the elements enumerated in 91—that is, with H, Cl, O, N, and C. Thus, platinum forms the saturated chloride $Pt\,Cl_4$, hence it is tetratomic, since chlorine is monatomic—the one atom of platinum replaces *four* atoms of hydrogen, for so much hydrogen would be required to saturate the four atoms of chlorine in the above chloride. Iron is tetratomic, because pyrite, Fe_2S, is a perfectly saturated compound; for sulphur forms the saturated H_2S, and is therefore diatomic. Consequently the S_2 here saturated by one atom of iron would saturate four atoms of hydrogen; in other words, one atom of iron replaces four atoms of hydrogen. Potassium is monatomic; for its chloride has the formula KaCl, or one atom of potassium replaces one atom of hydrogen in HCl.

97. In this manner the atomicity of most elements has been determined with a high degree of certainty. The following table gives the results:

univalent,	or *monatomic,*	are	Kaloids and Chloroids.
bivalent,	" *diatomic,*	"	Calcoids, Cadmoids, and Sulphoids.
trivalent,	" *triatomic,*	"	Phosphoids.
quadivalent,	" *tetratomic,*	"	Titanoids and Ferroids.

The members of the Cuproids appear not to have the same atomicitity: Ag is monatomic, Cu (and also Hg) is diatomic, and Au tetratomic.

98. The Ferroids at first sight appear to be trivalent; for they form well pronounced *sesquioxides*, such as ferric oxide, Fe_2O_3, and three atoms of bivalent oxygen represent six atomicities, consequently *three* for each of the two atoms of iron. But the vapor density of ferric chloride proves this compound to have the formula Fe_2Cl_6, or to contain *two* atoms of iron with *six* of chlorine, and not simply $FeCl_3$. But two atoms of iron combining would saturate at least one each of their atomicities, and since, besides this, six are left to hold the chlorine, the two atoms of iron, uncombined, must have eight atomicities; that is, Fe is tetratomic.

99. It is often quite convenient to *represent the atomicity by a roman numeral* at the upper right hand side of the chemical symbol. Thus, Fe^{IV} represents one atom of iron, supposed to be tetratomic; O^{II} represents a diatomic oxygen atom; R^{I} a monatomic radical, etc.

100. The same notation is often applied to compounds, and especially to compound radicals. Thus, water, H_2O, may be written HOH, so that *Hydroxyl*, $(OH)^{I}$, is a non-saturated, monatomic *radical*—that is, a group of atoms which will saturate, and therefore replace one atomicity. Why is NH diatomic, and CH triatomic?

Cyanogen,* Cy, is a negative compound radical of the formula CN; it is monatomic, since the triatomic, N, leaves one of the four atomicities of carbon unsaturated. Hence, hydrogen cyanide is HCy. (Chem. 193.)

Ammonium,† Am, is a positive compound radical of the formula NH_4; it is monatomic and positive, since the triatomic, N, leaves one of the four atomicities of hydrogen unsaturated. Hence, ammonium chloride is $AmCl = NH_4Cl$ (sal-ammoniac).

Ammonium hydroxyl will be $NH_4(OH)$, commonly called *ammonium hydrate.* By heat it will dissociate into the stable ammonia gas, NH_3, and steam, H_2O, according to—

$$NH_4OH + \text{heat} = NH_3 + H_2O$$

(Compare Chem. 140.)

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* Cyanogen is obtained in the free state as gas, by the dissociation of mercuric cyanide, exactly as oxygen is obtained from mercuric oxide. (Chem 99.) It is a colorless gas, of a pungent odor, resembling that of peach kernels; condensible to a liquid; burns with a beautiful purple flame, giving CO_2 and N. One cubic centimeter of cyanogen gas weighs 2.335 mgr at 0° and 760 mm, and dissolves in one-fourth its volume of water—hence it must be collected over mercury.

† Not yet prepared in the free state; its *amalgam* has been formed, *i. e.*, its alloy with mercury.

101. We may now unite, in one *systematic table* (Chem. 111), the symbols of the elements, together with the atomic weights and atomicities of the same. If the valence is the same for all species of a genus, we shall add the valence number to the symbol of the genus—otherwise to that of the species. (Compare 18.)

	SPECIES.				
GENERA.	I.	II.	III.	IV.	V.
$+K\alpha^{I}$	Li 7	Na 23	Ka 39	....	(Am 18)
$X\alpha^{II}$	....	....	Ca 40	Sr 87.6	Ba 137
$K\delta^{II}$	....	Mg 24	Zn 65.2	Cd 112	Pb 207
$\Upsilon\gamma^{II}$	....	....	....	....	Hg 200
$K\nu$	....	....	Cu^{II} 63.4	Ag^{I} 108	Au^{IV} 197
$\Sigma\iota^{IV}$	....	Al 27.4	Fe 56	Rh 104	Ir 198
$T\tau^{IV}$	C 12	Si 28	Ti 50	Pd 107	Pt 197.4
......	Bo^{III} 11	....	....	Sn^{IV} 118	....
Φ^{III}	N 14	P 31	As 75	Sb 122	Bi 210
Θ^{II}	O 16	S 32	Se 19.5	Te 128	....
$-X^{I}$	Fl 19	Cl 35.5	Br 80	Io 127	(Cy 26)
Υ^{I}	H 1	....	....	....	....
			VARIETIES.		
$\Sigma\delta^{IV}$	Cr 52	Mn 55	Fe 56	Ni 58	Co 60

102. In *simple* saturated *binary* compound, the *total valence* of the electro-positive element is equal to the total valence of the electro-negative element. Thus, in in H_3N the total valence is three for the electro-positive, and also three for the electro-positive.

In *complex* saturated binary compounds, the total valence of the negative differs from that of the positive according to the number of atomicities which are satisfied by atoms of the same element combining. Thus, in the saturated ferric chloride, Fe_2Cl_6, the total valence of the iron is 8, and that of the chlorine only 6, because the two iron atoms are united by one of their atomicities. (Compare 98.)

103. Simple binary compounds, containing less valence of the one element than of the other, are *not saturated*, and therefore not stable. Thus, ferrous oxide, FeO, stannous chloride, $SnCl_2$, carbonic oxide, CO, are unstable, because the electro-negative element represents only half as many atomicities as the electro-positive element. Such compounds have a very great tendency to combine with more of the electro-negative element; if they are oxides, they are reducing agents. (Compare Chem. 180.)

104. The same principles apply to *ternaries*, because they *may be considered as binarics, the electro-negative of which is a compound radical.* (See 100, where the radical cyanogen, $Cy^{I} = CN$, has been described; and carefully review Chem. 121 and 124.)

Thus, silver nitrate consists of Ag, O, and N (Chem. 125); it has the formula AgO_3N, already used in 29. But the group O_3N may be considered as a monovalent, negative, compound radical, which has combined with the monovalent positive radical silver. Accordingly, the formula of lead nitrate must be $Pb(O_3N)_2$, since Pb is bivalent. Ammonium nitrate is AmO_3N, or NH_4O_3N — hence its dissociation into $2\,H_2O$, and laughing gas, N_2O.

It is, of course, not necessary that these negative *radicals* do also possess an independent existence, uncombined with positive elements or radicals — *they simply represent groups of atoms which* DO *occur in compounds.* (Compare 41.)

Section V. Substitution.

105. One element can replace another in a compound if the valence remains the same; or, in *Substitution the total valence of the element introduced must be equal to the total valence of the amount of the element replaced.*

If in hydrogen chloride, HCl, the hydrogen is replaced by zinc, which is diatomic, the substitution takes place in two atoms of hydrogen chloride; and 2(HCl) + Zn will give zinc chloride, $ZnCl_2$, and a molecule of hydrogen gas, H_2. So, also, when potassium is thrown on water, one atom of the monovalent metal replaces one atom of the monovalent hydrogen, Ka + H_2O, giving KaOH + H; or, we may write: Ka + H(OH), giving potassium hydrate, Ka(OH), and hydrogen, H. (Compare Chem. 172, and 104.)

106. By observing this law of substitution, it is quite easy to write the formula of any salt, if the formula of corresponding hydrogen compound (*i. e.* the corresponding acid) is given. (Chem. 146.) Consequently, if the student once for all learns to apply this law, he need not remember the formulæ of the multitude of individual salts, but only the few formulæ of the corresponding acids. This is a point of exceeding great importance. We shall, therefore, give the formulæ of the principal acids, and expect the student to write the formulæ of the most important salts corresponding to these acids.

107. We shall append a *table* giving the formulæ of the principal inorganic acids, from which table the student must commit to memory those formulæ which represent the most common classes of salts. The student should construct the formulæ of the salts as these latter are exhibited by the teacher; besides, the student should give a definition of each group of salts here represented by one acid.

108. The definition can be read off from the formula of the acid. Thus, the formula of nitric acid being HO_3N, we define *Nitrates* as *ternaries* containing the *monovalent* electro-negative *radical*, O_3N. In like manner, hydric chloride being HCl, it follows that chlorides are binaries, containing the monovalent element Cl.

109. The general formula of any acid (Chem. 146) being $H_m \nu^m$, that is, containing m hydrogen atoms replaceable by other electro-positive atomicities, the negative must be m-valent, and the *general definition of the corresponding salts* will read:

$\nu \left\{\begin{matrix}\textit{ides}\\ \textit{ates}\end{matrix}\right\}$ *are* $\left\{\begin{matrix}\textit{bi-}\\ \textit{ter-}\end{matrix}\right\}$*naries containing the m-valent* $\left\{\begin{matrix}\textit{element}\\ \textit{radical}\end{matrix}\right\}$ ν *as the electro-negative.*

For example, phosphorous acid is H_3O_3P; but only two of the three atoms of hydrogen can be replaced by other electro-positive atomicities. Consequently, we must write $H_2(HO_3P)$, and define phosphites as ternaries containing the bivalent radical HO_3P as the electro-negative.

In practice, and for convenience of printing, the bracket around the constituent negatives may be omitted.

110. In writing the formulæ of salts, it should be borne in mind that—

Mn, Fe	are	bivalent	in	......ous	compounds.
Al_2, Mn_2, Fe_2	"	hexvalent	"	ic	"
Hg	is	bivalent	"	mercuric	"
Hg_2	"	bivalent	"	mercurous	"
Sn, Pt	are	bivalent	"	......ous	"
	and	quadrivalent	"	ic	"

111. It may also be well to observe that older works speak of *acid* salts and bi-salts, when only *one* hydrogen atom is replaced out of two or more. Thus, hydrogen sulphate being H_2O_4S, we have potassium sulphate, Ka_2O_4S, but also hydro-potassium sulphate, $HKaO_4S$, which latter, in older works, is called *bi-sulphate*, or acid sulphate. In the modern nomenclature such names are not required.

Section VI. System of Binaries and Ternaries.

112. After these explanations, the application of the following TABLE of formulæ of acids will not be difficult. This table, at the same time, gives an outline of *systematic chemistry* of compounds, as will be seen from the classification adopted. (See Chem. 119 to 128.)

113. I. BINARIES.*

ACID.	FORMULA.	WRITE FORMULA OF SALTS OF	NAME OF SALTS.
Hydrochloric	HCl	Na, Ka, Pb, Ag	*Chloride*
Hydrobromic	HBr	Na, Am, Cd	*Bromide*
Hydriodic	HIo	Ka, Ag, Fe^{ous}	*Iodide*
Hydrocyanic	HCy	Ka, Hg^{ic}, Ag	*Cyanide*
Hydrofluoric	HFl	Ca, Ag	*Fluoride*
H O^{ide}	H_2O	Pb, Fe, Hg	*Oxide* (114)
Hydrosulphuric	H_2S	Zn, Pb, Ag, Cu	*Sulphide* (115)
Hydroselenic	H_2Se	Pb	*Selenide*
Hydrotelluric	H_2Te	Pb	*Telluride*
H N^{ide}	H_3N	(many nitrides are explosive.)	*Nitride*
H P^{ide}	H_3P	gas; odor of rotten fish.	*Phosphide*
H As^{ide}	H_3As	gas; garlic odor	*Arsenide*
H Sb^{ide}	H_3Sb	gas; no odor	*Stibide*
H C^{ide}	H_4C	neutral gas	*Carbide*
H Si^{ide}	H_4Si	neutral gas	*Silicide*

114. II. OXYTERNARIES.

a. *Oxyhydroternaries.*

Hydric	$H(OH)$	Ka, Pb, Ba	*Hydrates*

b. *Oxychloroidternaries.*

Hypochlorous	$H(OCl)$	Na, Ka, Ca	*Hypochlorite*
Chlorous	$H(O_2Cl)$	Ka, Ba	*Chlorite*
Chloric	$H(O_3Cl)$	Ka, Ba, Ag	*Chlorate*
Perchloric	$H(O_4Cl)$	Ka, Ag	*Perchlorate*
Bromic	$H(O_3Br)$	Ka	*Bromate*
Iodic	$H(O_3Io)$	Ka	*Iodate*
Cyanic	$H(OCy)$	Ka, Ag	*Cyanate*

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* The *preparation* of the principal hydrogen binaries should be indicated as the acid or neutral compound is exhibited by the teacher. The most important of these are prepared as shown in Chem. 194, 193, 192. The hydrogen arsenide and stibide are obtained when a *small* quantity of the oxide is added to the contents of the hydrogen evolution flask. (Chem. 104.) Hydrogen phosphide is obtained in its *spontaneously inflammable* condition when a few small pieces of phosphorus are gently heated in concentrated potassium hydrate in a beaker on the sand-bath. A slight explosion and a flame is produced as the bubbles of phosphuretted hydrogen reach the air above the liquid.

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c. Oxysulphoidternaries.

Sulphuric	$H_2(O_4S)$	Ka, Ka_2, Al, Pb.	*Sulphate*
Sulphurous	$H_2(O_3S)$	Ka, Na_2, Na	*Sulphite*
Hydrosulphurous	$H(O_2HS)$	Na	*Hydrosulphite*
Hyposulphurous, or Dithionous	$H_2(O_3S_2)$	Na_2, NaH	*Dithionite*
Dithionic	$H_2(O_6S_2)$	———	*Dithionate*
Trithionic	$H_2(O_6S_3)$	———	*Trithionate*
Tetrathionic	$H_2(O_6S_4)$	———	*Tetrathionate*
Pentathionic	$H_2(O_6S_5)$	———	*Pentathionate*
Selenous	$H_2(O_3Se)$	Ka_2, Ag_2	*Selenite*
Selenic	$H_2O_4Se)$	———	*Selenate*
Telluric	$H_2(O_4Te)$	———	*Tellurate*

d. Oxyphosphoidternaries.

Pyrophosphoric	$H_4(O_7P_2)$	Na_4, Mg_2	*Pyrophosphate*
Phosphoric	$H_3(O_4P)$	Na_3, Ca_3, $\frac{Am}{Mg}$	*Phosphate*
Phosphorous	$H_2(HO_3P)$	Na, Ca	*Phosphite*
Hypophosphorous	$H(H_2O_2P)$	Na, Ca	*Hypophosphite*
Metaphosphoric	$H(O_3P)$	Na, Ca	*Metaphosphate*
Pyroarsenic	$H_4(O_7As)$	Mg	*Pyroarsenate*
Arsenic	$H_3(O_4As)$	AmMg	*Arsenate*
Arsenous	$H_2(HO_3As)$	Ka	*Arsenite*
Antimonic, or Stibic	$H_3(O_4Sb)$	Ka	*Antimonate, or Stibate*
Nitric	$H(O_3N)$	Ka, Pb, Ba	*Nitrate*
Nitrous	$H(O_2N)$	Ka	*Nitrite*

e. Oxytitanoidternaries.

Carbonic	$H_2(O_3C)$	Ka_2, Na_2, Ca	*Carbonate*
Oxalic*	$H_2(O_4C_2)$	Ka, Ca	*Oxalate*
Formic	$H(O_2HC)$	Ka	*Formate*
Acetic	$H(O_2H_3C_2)$	Ka, Pb, Ag	*Acetate*
Glycolic	$H_2(O_3H_2C_2)$	———	*Glycolate*
Lactic	$H_2(O_3H_4C_3)$	———	*Lactate*
Malonic	$H_2(O_4H_2C_3)$	———	*Malonate*
Succinic	$H_2(O_4H_4C_4)$	———	*Succinate*

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* **The following *organic acids* and salts contain a binary-hydro-carbon as negative element.**

Malic	$H_2(O_5H_4C_4)$	—	*Malate*
Tartric	$H_2(O_6H_4C_4)$	—	*Tartrate*
Citric	$H_3(O_7H_5C_6)$	—	*Citrate*
Orthosilicic	$H_4(O_4Si)$	Phenacites (Chem. p. 144).	*Orthosilicate*
Metasilicic	$H_2(O_3Si)$	Enstatites (Chem. p. 144).	*Metasilicate*

f. *Oxymetalloternaries*, unclassified.

Metaboric	$H(O_2Bo)$	—	*Metaborate*
Boric	$H_3(O_3Bo)$	Sassolite	*Borate*
Tetraboric	$H_2(O_7Bo_4)$	Na_2, Borax, 10 aq.	*Tetraborate*
Metatitanic	$H_2(O_3Ti)$	Ca-Perofskite	*Titanate*
Stannic	$H_2(O_3Sn)$	Na_2	*Stannate*
Plumbic	$H_2(O_3Pb)$	Ka_2	*Plumbate*
Molybdic	$H_2(O_4Mo)$	Wulfenite (Chem. p. 138).	*Molybdate*
Wolframic	$H_2(O_4Wo)$	(Chem. p. 138)	*Wolframate*
Chromic	$H_2(O_4Cr)$	Ka_2, Pb, Ba, Ag_2	*Chromate*
Bichromic	$H_2(O_7Cr_2)$	Ka_2	*Bichromate*
Manganic	$H_2(O_4Mn)$	Ka_2	*Manganate*
Permanganic	$H(O_4Mn)$	Ka	*Permanganate*
Ferric	$H_2(O_4Fe)$	Ka_2	*Ferrate*
Vanadic	$H_3(O_4Va)$	Vanadinite, contains Pb_3	*Vanadate*
Pyrovanadic	$H_4(O_7Va_2)$	in Descloizite, Pb_2	*Pyrovanadate*
Tantalic	$H_2(O_6Ta)$	Tantalite, Fe	*Tantalate*
Niobic	$H_2(O_6Nb)$	Columbite, Fe	*Niobate*
Dialuminic	$H_2(O_4Al_2)$	See the Minerals, gen. 81 to 84, Chem. pp. 136 to 138.	*Dialuminate*
Dichromic	$H_2(O_4Cr_2)$		*Dichromate*
Dimanganic	$H_2(O_4Mn_2)$		*Dimanganate*
Diferric	$H_2(O_4Fe_2)$		*Diferrate*

115. III. SULPHOTERNARIES.

Sulphhydrate	$H(SH)$	Ka, Am, Ca	
Sulphocyanate {or Rhodanate.}	$H(SCy)$	Ka, Fe_2	
Sulpharsenate*	R_1S_3As	Pyrargyrite, Ag	See Chem. p. 132–133.
Sulphostibate	R_1S_3Sb	Proustite, Ag	
Sulphobiarsenate	R_4S_7As	Tetrahedrite, Cu_4	
Sulphobistibate	R_4S_7Sb	Tennantite, Cu_4	
Sulphobiferrate	$R_2S_7Fe_2$	Chalcopyrite, Cu_2	

---

* Since many of the corresponding acids have not yet been prepared in the free state, we write the symbol R to represent a *monovalent* radical.

Sulphodiferrate.........$R_2S_4Fe_2$...Ka_2* Ag_2 } discovered
Sulphodibismuthate....$R_2S_4Bi_2$...Ka_2 } by Schneider.

When the freshly precipitated sulphides of As, Sb, Sn, Pt, Au, are, by washing, freed from adherent acid, and treated with yellow ammonium sulphide, they pass into solution, forming the corresponding ammonium sulpho-salts.

116. IV. CHLOROTERNARIES.

Chloroplatinate......R_2Cl_6Pt.....Am_2, Ka_2, tesseral (Phys. 190).
Chloropaladate......R_2Cl_6Pd.....Am_2, Ka_2, tesseral......
Chloroiridate..........R_2Cl_6Ir......Am_2, Ka_2, tesseral......
Chlorostannate.......R_2Cl_6Sn......Am_2, Ka_2, tesseral......
Chlorocadmiate......R_4Cl_6Cd.....Ka_4, hexag.; Am_4, rhomboh.
and many others.

117. V. BROMOTERNARIES.

Bromoplatinate......R_2Br_6Pt.....Am_2, Pb, tesseral.......

118. VI. IODOTERNARIES.

Iodoplatinate.........R_2Io_6Pt......Am_2, Ka_2, tesseral......

119. VII. CYANOTERNARIES.†

Cyano-ferrate ....R_4Cy_6Fe ...Ka_4 (yellow prussiate of potassa, containing 3 H_3O).
Cyani-ferrate ....R_3Cy_6Fe ...Ka_3 (red prussiate of potassa.)...............
Cyani-chromate......R_3Cy_6Cr ...Ka_3...........................
Cyani-manganate....R_3Cy_6Mn...Ka_3...........................
Cyani-cobaltate......R_3Cy_6Co....Ka_3...........................
Cyano-platinate......R_2Cy_4Pt ....Ba, Mg......................

120. VIII. FLUOTERNARIES.

Fluoaluminate........R_3Fl_6Al.....Na_3, Cryolite, (Chem. p. 158.)......
Fluosilicate...........R_2Fl_6Si......H_2‡, Ka_2, Ba..............
Fluotitanate...........R_2Fl_6Ti......Am_2, Na_2.....................
Fluostannate ....R_2Fl_6Sn .....Am_2, Na_2.....................

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* Remains upon treating the fused mass of one part of iron, six parts of potassium carbonate, and six parts of sulphur. The others are prepared in a similar manner

† For the sake of convenience, the endings o and i are retained from the older terminology. Thus, ferro-cyanide of .... is cyano-ferrate, and ferri-cyanide of .... is cyani-ferrate. (Chem. 180.)

‡ The hydrogen fluo-silicate is, in older works, called hydro-fluosilicic acid. It is obtained in solution by passing into water the silicon fluoride gas $SiFl_4$ evolved

121. IX. ISOMORPHOUS HYDRATED SALTS can be represented by a general formula.* The crystal form remains the same for the same atoms of water of crystallization, but changes with the latter. (Chem. 92.)

For the sake of brevity, we shall represent one atom of water of crystallization by aq, the abbreviation of aqua. Hence —

$$aq = H_2O$$

122. From the very great number of such isomorphous groups, we shall select only the following:

NAME, OR DISCOVERER.	FORMULA.	SPECIES—R BEING
Epsomites	$R''O_4S + 7\ aq$	Mg, Zn, Fe
Chalcanthites	$R''O_4S + 5\ aq$	Cu
———	$\genfrac{}{}{0pt}{}{Am}{Mg}O_4\Phi + 6\ aq$	P, As
(Marignac)	$R''Fl_6Si + 6\ aq$	Ni, Cu, Zn, Cd; Ag_2
(Marignac)	$R''Fl_6Ti + 6\ aq$	Mg
(Marignac)	$R''Fl_6Sn + 6\ aq$	Ni, Mn, Mg, Zn; Ag_2
(Bonsdorff)	$R''Cl_6Pt + 6\ aq$	Mg, Zn, Cd; Mn, Fe, Ni,
(Bonsdorff)	$R''Cl_6Pt + 12\ aq$	Mg, Mn [Co; Cu.
(Topsoe)	$R''Br_6Pt + 6\ aq$	Ni; Na_2
(Topsoe)	$R''Io_6Pt + 6\ aq$	Ni
(Topsoe)	$R''Br_6Pt + 12\ aq$	Mg, Zn, Mn, Co; Ca
(Topsoe)	$R''Io_6Pt + 12\ aq$	Ca
(Topsoe)	$R''Io_6Pt + 9\ aq$	Mg, Zn; Mn, Fe, Ni, Co
———	$R''Cy_4Pt + 4\ aq$	Mg,† Ba
———	$R'''Cy_6Fe + 3\ aq$	Ka_4

123. X. ISOMORPHOUS HYDRATED DOUBLE SALTS.— Prominent among these are the,—

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by the gentle heating of a mixture of quartz, SiO_2, and fluorite, $CaFl_2$, with concentrated sulphuric acid. The tube conducting the gas into the water should be very wide, as fluocculent hydrogen silicate separates.

* Here R', R'', R''', etc., represent monatomic, diatomic, triatomic elements or radicals.

† The crystals of the magnesium compound show *dichroism* in the highest degree —being red in the direction of the axis, and bluish green at right angles thereto. (Compare Chem. p. 153, No. 17, and p. 136, gen. 81, spec. I., var. b.)

a. *Haueroids:* $Ka_2O_4S + R''O_4S + 6$ aq, wherein
$Ka = Ka$, Am, and
$R'' =$ Mg, Zn, Cd, Cu, Co, Ni, Fe, Mn.
(See Phys. 178, 195, 196, for the description of this, perhaps the most instructive of groups.)

b. *Alums:* $Ka_2O_4S + \Sigma\iota_2(O_4S)_3 + 24$ aq, wherein
$Ka = Ka$, Am, etc.
$\Sigma\iota =$ Al, Fe, Cr. (See Phys. 190, 194.)

Section VII. Serial Radicals.

124. The same principles of *substitution* (see 105) which enable us to determine the formula of a salt from that of the corresponding acid given in the preceding paragraphs, will permit us to construct the formulæ of a large majority of the so-called *organic* or *serial compounds.* (Chem. 119, 127.) In fact, the principles of substitution were originally deduced from the observed facts of organic chemistry.

125. The binary marsh gas (48), also called *methane,* CH_4, is the basis of all organic compounds. It is saturated, the valence of four monovalent hydrogen atoms completely satisfying the quadrivalent carbon atom. But if one atom of hydrogen be removed, the compound monovalent radical, $CH_3 = Me$, called *methyl,* would result.

126. Methyl does not exist as single molecule, or in the free state. It is only known in combination with other radicals (itself included, see 130), or with elements.

The following *table* gives a few of the resulting compounds, together with the boiling point, t. of the same. The student should write the formulæ *in full.**

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* Thus, the MeCy is CH_3 CN, composed of the monovalent positive radical Me and the monovalent negative radical Cy.

t° C.	NAME.	FORMULA.	REMARKS.
?	Methyl hydride	MeH	Marsh gas; never liquefied as yet.
—21	“ chloride	$MeCl$	Gas; condensed at —21°.
13	“ bromide	$MeBr$	Liquid.
43	“ iodide	$MeIo$	Liquid.
66	“ nitrate	MeO_3N	Vapor explodes at 150°*.
?	“ bisulphate	$MeHO_4S$	Colorless crystals. (See 111.)
188	“ sulphate	Me_2O_4S	Liquid.
—21	“ oxide	Me_2O	Methylether, gas.
66	“ hydrate	$MeOH$	Methylalcohol, or wood spirits.
58	“ cyanide	$MeCy$	Strong odor; vapor
?	“ carbonylamine	$MeNCO$	Very volat. liq.
133	“ sulphocyanate	$MeSCy$	
119	“ sulphocarbonylamine	$MeNCS$	Cryst. fuse, 34°.
?	“ amine	$MeNH_2$	Gas, easily liquefied.
8	Dimethylamine	Me_2NH	Gas, liquefied at 8°.
9	Trimethylamine	Me_3N	Gas, liquefied at 9°.
?	Tetramethylammoniumiodide	Me_4NIo	White crystals.
?	Tetramethylammoniumhydrate	Me_4NOH	
120	Trimethylarsine	Me_3As	Colorless liquid.
?	Tetramethylarsoniumiodide	Me_4AsIo	Crystal.
——	Tetramethylarsoniumhydroxide	Me_4AsOH	Crystal.
100	Arsendimethylchloride	Me_2AsCl	
170	Arsendimethyl.	$Me_2AsAsMe_2$	Cacodyl.†
135	Arsenmonomethylchloride	$MeAsCl_2$	Liquid.
——	Arsenmonomethyloxide	$MeAsO$	Crystal; odor of asafœtida.
——	Bormethyl	Me_3Bo	Gas; burns in contact with air.
——	Zincmethyl	Me_2Zn	Liquid; spontaneously inflammable.
95	Mercurmethyl	Me_2Hg	Liquid; exceedingly poisonous.

---

* The able chemist Chapman, his assistants, and the building in which they experimented, were blown to atoms by this substance in 1872.

† This liquid has a terrible odor. It burns in contact with atmospheric air at common temperature. All these arsenic compounds are very dangerous. A mixture of potassium (or sodium) acetate and arsenous oxide gently heated in a test-tube, yields cacodyl. Use only very little of the oxide. Avoid all moisture.

127. In writing out the full formulæ of these compounds, the valence of the constituent radicals must be borne in mind. Thus, evidently, the—

radical	OH,	*hydroxyl,*	is monovalent;
"	CO,	*carbonyl,*	" divalent;
"	CS,	*sulphcarbonyl,*	" divalent;
"	NH_2,	*amidogen,*	" monovalent;
"	NH,	*imidogen,*	" divalent;
"	NO_2,	*nitryl,*	" monovalent.

The *reason* for this valence is to be given by the principles of 102. The arsenic compounds correspond to the nitrogen compounds. The tetramethyl ammonium is seen to correspond to ammonium (100), each hydrogen atom in the latter being replaced by a methyl atom.

128. But the methyl radical CH_3 being compound, may itself undergo changes by substitution; and these substitution products may again enter in any of the above compounds. Thus, we have:

—	Methane = Methylhydride........MeH	$= CH_3H$	See 126.
—	Chlormethane..MeCl	$= CH_3Cl$	
41	Bichlormethane	CH_2Cl_2............	Liquid.
62	Trichlormethane	$CHCl_3$	Chloroform.
77	Tetrachlormethane......	CCl_4...............	
152	Tribrommethane	$CHBr_3$............	Bromoform.
—	Triiodomethane..........	$CHIo_3$............	Iodoform; yellow crystals.
112	Nitrotrichlormethane ...	$C(NO_2)Cl_3$	Nitrochloroform, or Chloropicrine.
—	Trinitromethane..........	$CH(NO_2)_3$.........	Nitroform; crystal.
—	Tetranitromethane......	$C(NO_2)_4$	
—	Formaldehyde............	CH_2O.............	Gas; Methylaldehyde.
—	Methylcyanide. MeCy	$= CH_3 \cdot Cy =$ *Acetonitrile.*	
—	Nitroacetonitrile.........	$Cy \cdot C(NO_2)H_2$...	Not yet prepared.
—	Mercuricfulminate	$Cy \cdot C(NO_2)Hg$..	In percussion caps.

129. The formaldehyde last mentioned is properly the oxymethane, and really the starting point for a great number of compounds, commonly called the *formyl compounds;* for the above may be considered formylhydride, if the compound monovalent negative radical—

$$\textit{Formyl} = Fo = COH.$$

We enumerate the following compounds:

——	Formylhydride	FoH	Formylaldehyde of 128.
100	Formylhydroxyl	$FoOH$	Formic acid.
	or, *Hydrogen Formate*	$HOFo$	
——	Ammonium Formate	$AmOFo = NH_4O\,COH$	
——	Lead Formate	$Pb(OFo)_2$	
——	Mercurous Formate	$Hg_2(OFo)_2$	etc.
33.4	Methylformate	$MeOFo$	Ethereal liquid.
194	Formamide	H_2NFo	

and multitudes of other compounds. The full formulæ should be written out by the student.

130. But if methyl is a monatomic radical, deporting itself exactly as an element, its molecule in the free state ought to consist of two atoms, mutually satisfying their valence, precisely as for the monatomic elements H, Cl, Br, etc., in the gaseous condition, have the molecules Cl_2, Br_2, etc. In other words, the radical methyl *ought* to be unknown as Me, but ought to occur as Me_2; that is, $CH_3CH_3 = C_2H_6$. (Compare 126.)

Now this substance is very well known as a *gas*,* called *Ethane.* It is a saturated compound, since the two methyl atoms mutually saturate one another. Hence, from ethane a new monovalent compound radical, *ethyl*, arises, by the removal of one atom of hydrogen.

131. This monovalent ethyl-radical, $Et = CH_2CH_3 = C_2H_5$, is the starting point of another group of compounds, much more numerous even than those of the radical methyl. We enumerate the following, for which the student should write the full formulæ by replacing the value of the symbol. At the same time, the student should try to ascertain how far the law in regard to the neutralization of the atomicities is complete. (See 102, and bear in mind 127.)

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* Occurs in common illuminating gas.

78.4	Ethylhydroxyl	EtOH	Ethylalcohol, common alcohol.
or,	Hydrogen ethylate	HOEt	
——	Sodium ethylate	NaOEt	
——	Potassium ethylate	KaOEt	
12.5	Ethylchloride	EtCl	Gas.
40	Ethylbromide	EtBr	Liquid.
72	Ethyliodide	EtIo	
34.5	Diethyloxide	Et_2O	Ether (sulphuric ether).
12	Ethylmethyloxide	EtMeO	A mixed ether.
86	Ethylnitrate	EtO_3N	Nitric ether.
16.5	Ethylnitrite	EtO_2N	Nitrous ether.
——	Ethylperchlorate	EtO_4Cl	Exceedingly explosive liquid.
——	Ethylhydrosulphate	$EtHO_4S$	Dissociates before ebullition
——	Ethylsulphate	Et_2O_4S	
160	Ethylsulphite	Et_2O_3S	
215	Triethylphosphate	Et_3O_4P	
——	Diethylphosphate	Et_2HO_4P	
——	Ethylphosphate	EtH_2O_4P	

Etc., etc., the phosphite, arsenate, arsenite, borate, silicate, carbonate, and others.

55	Ethylformate	EtOFo	Ethylformic ether.
77	Ethylcyanide	EtCy	Ethylcarbylamine; poisonous.
——	Ethylcyanate	EtOCy	Non-volatile liquid
146	Ethylsulphocyanate	EtSCy	
18.7	Ethylamine	EtH_2N	
57	Diethylamine	Et_2HN	
89	Triethylamine	Et_3N	
——	Tetraethylammonium-iodide	Et_4NIo	Crystals.
——	Tetraethylammonium-hydroxyl	Et_4NOH	
25	Ethylphosphine	EtH_2P	
85	Diethylphosphine	Et_2HP	
127.5	Triethylphosphine	Et_3P	

——	Tetraethylphosphonium-iodide	Et_4PIo	White crystals.
140	Triethylarsine	Et_3As	Not spontaneously inflammable.
190	Arsendiethyl	$Et_2AsAsEt_2$	Spontaneously inflammable.
158	Triethylstibine	Et_3Sb	
——	Triethylbismuthine	Et_3Bi	
——	Triethylborine	Et_3Bo	
36	Ethylhydrosulphide	$EtSH$	Mercaptan; Sulph-alcohol.
or,	Hydrogen sulphethylate	$HSEt$	
——	Mercuric sulphethylate	$Hg(SEt)_2$	
91	Ethyl sulphide	Et_2S	Have very bad odor.
——	“ selenide	Et_2Se	
——	“ telluride	Et_2Te	
118	Zincethyl	Et_2Zn	Spontoneously inflammable in air.
159	Mercuric ethyl	Et_2Hg	Not spont. inflam-Very poisonous.
150	Silicic ethyl	Et_4Si	
181	Stannic ethyl	Et_4Sn	
——	Tin triethyl	$Et_3Sn_2Et_3$	
——	“ diethyl	$Et_2Sn_2Et_2$	
200	Lead tetraethyl	Et_4Pb	

132. Precisely as formyl resulted from methyl by the substitution of H_2 by O, so acetyl, $Ac = C_2OH_3 = COCH_3$, results from ethyl $= Et = C_2H_3 = CH_2CH_3$. (See 131, 129.) Of the innumerable compounds, we mention:

21	Acetylhydride	AcH	Aldehyde.
118	Acetylhydroxyl	$AcOH$	Acetic acid.
or,	Hydrogen acetate	$H(OAc)$	
——	Sodium “	$NaOAc$	Cryst. with 3 aq.
——	Ammonium “	$AmOAc$	
——	Lead “	$Pb(OAc)_2$	Cryst. with 3 aq as Sugar of Lead.
——	Basic Lead “	$Pb(OAc)(OH)$	Lead Vinegar.
——	Copper “	$Cu(OAc)_2$	Cryst. with 1 aq.
——	Silver “	$Ag(OAc)$	
55	Methyl “	$Me(OAc)$	
74	Ethyl “	$Et(OAc)$	

55	Acetyl chloride	$AcCl$	
81	" bromide	$AcBr$	
108	" iodide	$AcIo$	
138	" oxide	Ac_2O	Acetic anhydride.
121	" sulphide	Ac_2S	
93	Thiacetic acid	$AcSH$	See acetic acid.
222	Acetamide	AcH_2N	White crystals. Fuse 78°.
——	Silveracetamid	$AcAgHN$	
——	Diacetamid	Ac_2HN	Crystal. Fuse 74°.
——	Triacetamid	Ac_3N	Crystal. Fuse 78°

133. The following chloroid substitution product may yet be mentioned:

?	Ethane	C_2H_6	
12.5	Chlorethane	C_2H_5Cl	
65	Dichlorethane	$C_2H_4Cl_3$	
75	Trichorethane	$C_2H_3Cl_3$	
102	Tetrachlorethane	$C_2H_2Cl_4$	
146	Pentachlorethane	C_2HCl_5	
182	Hexachlorethane	C_2Cl_6	Colorless crystal.

——	Acetic acid	$H\text{-}O\text{-}C_2H_3O$	See 132.
158	Monochloracetic acid	$H\text{-}O\text{-}C_2H_2ClO$	Crystal. Fuse 62
143.5	Ethylmonochloracetate	$EtOC_2H_2ClO$	
195	Dichloracetic acid	HOC_2HCl_2O	Crystal.
——	Trichloracetic acid	HOC_2HCl_3O	
99	*Chloral*	HOC_2Cl_3	i. e., aldehyd of preceding.
——	*Chloralhydrate*	HOC_2Cl_3HOH	Crystal.
208	Monobromacetic acid	HOC_2H_2BrO	Crystal. Fuse b low 100°.
225	Dibromacetic acid	HOC_2HBr_2O	
245	Tribromacetic acid	HOC_2Br_3O	Crystal 130.
——	Cyanacetic acid	HOC_2H_2CyO	Crystal.

134. The radical atom ethyl, $Et = C_2H_5$, does no exist free, as little as O or H (see 130); but combine with Me or Et, result:

Methylethyl, MeEt = $CH_3 . C_2H_5 = C_3H_8$ = Propane.
Ethylethyl, EtEt = $C_2H_5 . C_2H_5 = C_4H_{10}$ = Quartane.

From each of these again follows a monatomic radical, if H be removed, namely:

Propyl = C_3H_7 = Pr
Butyl = C_4H_9 = Bu

Each of these radicals is again the centre of a great group of compounds, precisely as Me and Et. But they cannot occur free — they will give:

Pr-Me = C_3H_7-CH_3 = C_4H_{10} = Quartane.
Pr-Et = C_3H_7-C_2H_5= C_5H_{12} = Quintane.
Bu-Et = C_4H_9-C_2H_5= C_6H_{14} = Hexane.

From these again follow the new monatomic radicals —

Amyl = C_5H_{11}, and Hexyl = C_6H_{13}.

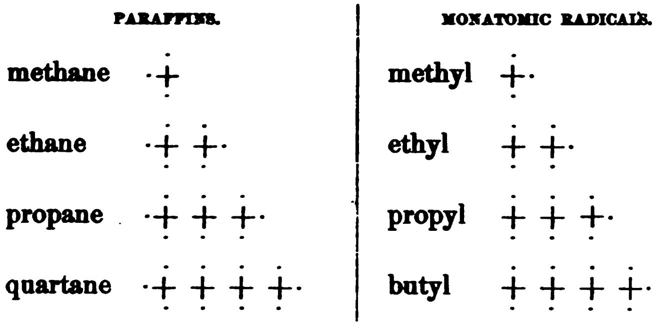
These again combining with any of the preceding, lead to radicals of a still higher number of carbon atoms.

The *general formula* for the monatomic radical of hydrocarbon containing n atoms is evidently C_nH_{2n+1}. The corresponding saturated hydrocarbon is C_nH_{2n+2}. These latter are called *Paraffins.*

135. In view of these facts, it is impossible to resist the conclusion that these *paraffins are true serial compounds*, consisting of a certain number, n, of diatomic methane radicals, CH_2, each one linked to the preceding and succeeding by one of the two atomicities unsatisfied; and that at each end of this series the atom-string is closed by an atom of hydrogen. (Compare Chem. 119.) Thus, methane is HCH_2H, ethane HCH_2CH_2H, and, in general, the nth paraffin is $H(CH_2)_nH$.

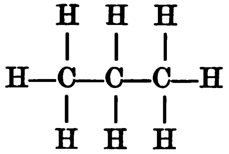
Section VIII. Chemical Constitution.

136. These facts can be best represented *graphically*, if the quadrivalent carbon atom be represented by a cross or plus sign, and the univalent hydrogen by a dot or period. Thus result the following *graphical formulæ:*



137. This method of representation we have introduced in the place of the so-called *developed structural formulæ*, which require the use of the common chemical symbols, each provided with as many *lines*, *bonds*, or *hands* as the corresponding atom has atomicities. For example:

propane.................



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

although a very simple case, gives the very slowly-written and difficultly-printed developed structural formula here presented.

It will also be noticed, that our symbol for carbon is really obtained by a simple *contraction* of the four lines into a small cross, and the omission of the letter C.

138. The great practical convenience of this representation has lead us to represent O and N in a like manner. The divalent oxygen atom we represent by a *dash* (—), the two extremities of which represent its centres of attraction, or poles, or atomicities. The trivalent nitrogen atom is represented by a *tri-cornered star* (⅄), easily drawn by pen or chalk, in three curves—the three corners indicating the three atomicities of the atom. Finally, the monatomic chlorine occuring so frequently, we represent it by a *comma* (-), the point being the centre of attraction of the same in combinations.

139. The following, accordingly, presents our *graphical symbols* of the five elements most common in serial compounds — symbols expressive of the *valence* or atomicity of the atoms of these elements :

Cl	-	monatomic, or univalent.
H	•	monatomic, or univalent.
O	—	diatomic, or divalent.
N	Y	triatomic, or trivalent.
C	+	tetratomic, or quadrivalent.

(See Plate I., fig. 1, line B.)

140. These same symbols, *open*, represent other elements of the same atomicity. An open comma stands for any univalent electro-negative; an open point, or circle, for any univalent electro-positive atom; an open three-sided star, for any trivalent atom; and an open four-sided star, for any quadrivalent atom. (See Plate I., fig. 1, line A.)

But very rarely more than one of these occurs in any formula; hence it will not often be necessary to add some further distinction mark, such as a point, in the middle of these open figures.

141. In figure 1, Plate I., column 0 (*i. e.*, atomicity zero, *saturated compounds*), the four typical compounds, HCl, H_2O, H_3N, and H_4C, have been represented graphically in this manner, in lines C, D, E, and F. In column 1, comprising *univalent* elements and radicals, we find, in line D, hydroxyl, OH; in line E, amidogen, H_2N; in line F, methyl, H_3C; in line G, the positive ammonium, $Am = NH_4$, and the negative cyanogen, $Cy = CN$; in line H, nitryl, NO_2.

In column 2, we find the *divalent* elements and radicals — in line E, imidogen, HN; in line F, methene, CH_2; in line G, carbonyl, CO.

In column 3, we the trivalent elements and radicals. Thus, in line F is methenyl, CH.

In column 0, line K, we find the very convenient compound symbol for benzol, C_6H_6, where the six carbon atoms are represented by two three-sided stars crossing one another. To the right of this symbol the univalent phenyl, C_6H_5, has been represented.

Besides, we find, in fig. 1, the graphical formulæ of chloroform (H, 0), Me = methyl (K, 2), Fo = formyl (H, 2), Et = ethyl (K, 3), Ac = acetyl (H, 3).

142. A large majority of the compounds enumerated in the preceding tables (126, 128, 129, 131, 132), should now be graphically constructed by the student. As examples, we give, in fig. 2, under A, alcohol; B, acetic acid; C, ether; D, methyl acetate; E, trimethylamine.

In these constructions, it is essential to constantly bear in mind not simply the laws of atomicity, but also the facts of *constitution* represented in the formulæ before given and established experimentally by the *reactions* of the substance.

143. It will have been noticed that the chemical formulæ used in the preceding section, and in the last articles, are very different from those we employed in section VI. In the chemical formulæ just studied, not only the *number* and *kind* of element-atoms is expressed, but also the *manner* in which these atoms are united, is indicated. As the manner in which the element-atoms are united in a compound-atom became gradually apparent to the eye of the chemist, the formula expressing this mode of combination gradually changed, becoming more and more *specialized.* The various formulæ thus resulting will now be explained, in the *order* in which they were evolved by chemical research.* As examples, we shall make use of the compounds: alcohol, ether, and acetic ether.

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* These formulæ do not conflict, as supposed by superficial historians of chemistry. They differ in such a manner, that the more general and earlier formulæ constantly embrace the more specialized and later formulæ, resulting from a more thorough knowledge of the compounds.

144. *The* EMPIRICAL FORMULA *of any compound simply expresses the number of atoms of each of the different constituent elements contained in* ONE *atom of the compound.* (Compare 16.)

Thus, the empirical formula of alcohol is C_2H_6O; of ether, $C_4H_{10}O$; and of acetic ether, or ethyl acetate, $C_4H_8O_2$.

This formula may also properly be considered the *molecular formula* of the compound. In that case, the *empirical* formula, properly so called, will simply express the percentage of composition in the lowest possible number of atomic weights. Thus, the empirical formula proper of ethyl acetate would be C_2H_4O, while the above given formula represents *one molecule*, or atom, of this compound.

145. These formulæ assert absolutely *nothing* in regard to the manner in which the constituent atoms are united in the compound atom. The empirical or molecular formula, therefore, will be known if we ascertain:

a. By *chemical analysis*, the quantitative percentage composition of the compound — that will give the *ratio* of the number of atoms of the different elements in a compound, or the *empirical* formula proper; and,

b. By means of a determination of the molecular weight (54), find the entire atomic weight, or the *sum* of the number of element-atoms in one atom of the compound — thereby the *molecular* formula proper results.

For example: pure alcohol consists, according to its analysis (Chem. 158), of 52.18 per cent carbon, 13.04 per cent hydrogen, and 34.78 per cent oxygen. If the number of oxygen atoms in one atom of carbon be called n, then one atom of alcohol contains 6.n atoms of hydrogen, and 2.n atoms of carbon, according to this percentage composition. Consequently, the weight of one atom of alcohol will be equal to 2.nC + 6.nH + nO, which is 46.n. But by the determination of its molecular weight, we find the milligram molecule to weigh 46 mgr; hence we have 46.n = 46, and consequently n = 1, which gives the empirical formula C_2H_6O.

146. *The* RADICAL FORMULA *of a compound represents the proximate radicals of which the atom of the compound is* (or appears to be) *composed.*

Thus, in alcohol the radical ethyl, Et = C_2H_6, is contained; hence the radical formula of alcohol is EtOH, which again may be written in full, $(C_2H_5)OH$. (Compare 131.) In a like manner, the radical formula of ether is Et_2O, or $(C_2H_5)_2O$, and that of ethyl acetate is EtOAc, or, in full, $(C_2H_5)O(C_2H_3O)$. (Compare 104.)

147. The radical formula can, of course, only be determined when also the *reactions* of the substance have been carefully studied, after the empirical formula has been established. Thus, the action of various chemicals on alcohol gives rise to the compounds enumerated in 131—they have all in common the group Et = C_2H_5, which, therefore, seems to have remained *unchanged* in all these processes; hence it is called the radical of alcohol.

184. It is therefore apparent that the radical formula expresses *more* particulars than the empirical formula; hence it is evident that different radical formulæ may correspond to the same empirical formula.

Substances, which are different, but possess the same empirical formula, are said to be isomeric; they have, therefore, different radical formulæ.

149. Among serial compounds, isomerism is very frequent. A very simple and striking example we have in *methyl acetate*, MeOAc (see 132), and *ethyl formate*, EtOFo (131). The empirical formula of both of these compounds is the same, $C_3H_6O_2$; but, when distilled with potassium hydrate, the former yields methyl alcohol as distillate, and potassium acetate as residue, while the latter yields common ethyl alcohol as distillate, and potassium formate as residue — and by this reaction the above radical formulæ are established (supposing, of course, the empirical formula to be known). Propionic acid, $C_3H_5O\text{-}OH$, gives potassium propionate, $C_3H_5O\text{-}OKa$, with potassium hydrate, it is the third isomeric of the above empirical formula, $C_3H_6O_2$.

150. *The* TYPICAL FORMULA *of any compound is obtained by writing its radical formula in accordance with one of the following four* TYPES *of modern chemistry:*

Hydrochloric-type.	Water-type.	Ammonia-type.	Methane-type.
$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$

(See 47, 48; 91 to 94.)

For greater convenience in printing, we shall print the four types thus:

Hydrochloric-type.	Water-type.	Ammonia-type.	Methane-type.
$\begin{matrix}H\\H\end{matrix}$	$\begin{matrix}H\\H\end{matrix}O$	$\begin{matrix}H\\H\end{matrix}N\,H$	$\begin{matrix}H\\H\end{matrix}C\begin{matrix}H\\H\end{matrix}$

This form will afterwards be found more correct than the commonly-used form given above.

151. The following *examples* will make the signification and use of these typical formulæ more familiar:

TYPE.	NAME OF COMPOUND.	TYPICAL FOMULÆ	
		Radical.	*In full.*
I. *Hydrochloric.*	Ethyl cyanide...........	$\begin{matrix}Et\\Cy\end{matrix}$	$\begin{matrix}C_2H_5\\CN\end{matrix}$
	Ethyl hydride...........	$\begin{matrix}Et\\H\end{matrix}$	$\begin{matrix}C_2H_5\\H\end{matrix}$
II. *Water.*	Alcohol.....................	$\begin{matrix}Et\\H\end{matrix}O$	$\begin{matrix}C_2H_5\\H\end{matrix}O$
	Ether	$\begin{matrix}Et\\Et\end{matrix}O$	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$
	Ethyl acetate............	$\begin{matrix}Et\\Ac\end{matrix}O$	$\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}O$
III. *Ammonia.*	Ethyl-methyl-amine..	$\begin{matrix}Et\\Me\end{matrix}N\,H$	$\begin{matrix}C_2H_5\\CH_3\end{matrix}N\,H$
IV. *Methane.*	Trimethylcarbinol.....	$\begin{matrix}Me\\Me\end{matrix}C\begin{matrix}Me\\OH\end{matrix}$	$\begin{matrix}CH_3\\CH_3\end{matrix}C\begin{matrix}CH_3\\OH\end{matrix}$

152. The only *real advantage* obtained by the employment of the typical formulæ is the greater clearness, bringing the constituent radicals more plainly into view, because each one is usually in a separate horizontal line.

153. We are well aware of the fact that many formulæ are considered typical ones, although they do not correspond to the definition given in 150; but it will be found that such formulæ represent no well established principle at all. Such results of fancy, which mar the pages of many a modern treatise of chemistry, will soon be referred to only as historical warnings.

154. To give a single example, we copy from modern treatises the formula of hydrogen phosphate on the type of three water atoms — that is, $\left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3$. But this formula rests upon no reactions experimentally established — it is simply the result of fancy applied to the empirical formula H_3O_4P, restrained only by the known valence of H, O, and P.* All that is chemically known in regard to the arrangement of the atoms in phosphoric acid is, that it contains three replaceable hydrogen atoms, or that its formula is on the ammonia type, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}O_4P$, the three-atomic radical PO_4 replacing N. How completely this harmonizes with the typical formula of phosphuretted hydrogen, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$, will be shown in the sequel. (Compare 113.)

155. *The* STRUCTURAL FORMULA *of a compound results from the radical formula by resolving the radicals again into their constituent radicals.*

Thus, ethyl, $Et = C_2H_5$, is, according to its genesis, CH_2CH_3, and acetyl, $Ac = C_2H_3O$, is, according to its genesis, $COCH_3$ (see 130 to 137). Consequently, the formula of—

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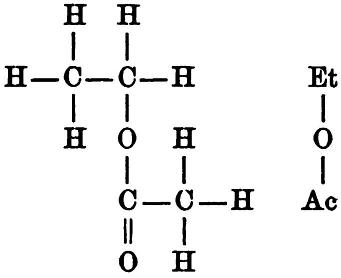
* The valence of P is assumed to be five — in reality it is only three. (See 97.)

alcohol is $H\text{-}O\text{-}CH_2\text{-}CH_3$;
ether " $CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$;
ethyl acetate " $CH_3\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_3$.

156. *The* DEVELOPED STRUCTURAL FORMULA results by developing each of the sub-radicals of the structural formula in accordance with the atomicities of its constituents.

Besides the example of propane given in 137, we give here the developed structural formula of ethyl acetate, arranged in such a manner as to permit its being printed by common types. A guide or clue has been added to the right, to aid the student. This one example is undoubtedly sufficient.



$$\begin{array}{cccccccccc}
 & & H & & H & & & & & \\
 & & | & & | & & & & & \\
H & — & C & — & C & — & H & & & Et \\
 & & | & & | & & & & & | \\
 & & H & & O & & H & & & O \\
 & & & & | & & | & & & | \\
 & & & & C & — & C & — & H & Ac \\
 & & & & \| & & | & & & \\
 & & & & O & & H & & &
\end{array}$$

157. *Our* GRAPHICAL FORMULÆ *result when these clumsy structural formulæ are written by our symbols* (explained in 136 to 142). Thus, the figure 3 is the graphical formula of ethyl acetate, and expresses all the facts and principles involved in the unwieldly formula printed in 156. For additional examples, see Plate I.

158. *The* STEREOGRAPHIC FORMULA *of a compound is an axonometric drawing of the atom* (Compare Phys. 76. Example, Ethane, C_2H_6, in fig. 4.)

In general, our graphical formula is the horizontal projection of the atom (Phys. 75), enabling us to determine the two co-ordinates x, y, of each atom in the compound atom. The third co-ordinate, z, is read off in the stereographic formula. (Compare Phys. 71 to 74.)

159. It is evident that the true stereographic formula is the formula most difficultly determined. Many chemists pronounce the determination of such formulæ impossible; but in our *Molecular Mechanics* this problem is solved for a number of compounds, according to the principles first published by us in 1867.* Here it is quite sufficient to insist on these facts, since the *details*, necessarily, are a speciality. (See 4.)

160. All the formulæ defined in 146, 150, 155, 156, and 157 are called *rational formulæ*, and are distinguished as such from the empirical formulæ of 144. These formulœ are properly called rational, because they are necessarily based upon a rational knowledge of the physical and chemical properties of the compound.

161. The quantitative analysis of a compound gives us only the percentage composition and the *relative* number of atoms of the constituent elements in the atom of the compound — expressible by the empirical formula proper. The molecular weight of the vapor thereafter gives the *absolute* number of these atoms, thus determining the molecular formulæ. (See 145.)

The study of the chemical reactions of the compound will thereafter reveal the radical formula of the same (146 to 149), which may be written *typically* (150 to 152), for the sake of greater perspicuity.

A thorough study of the substitution products of the compound and its radicals will now lead to the establishment of the developed structural formula (155, 156).

A rather difficult mathematical study of the physical properties (specific heat, boiling point, etc.) will finally lead to the knowledge of the true graphical, and even the stereographical, formula of the compound — as will be shown in our special treatise on *Molecular Mechanics*. (See 157 to 160.)

162. Thus, it appears that the true *chemical constitu-*

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* Atomechanik, 1867. Comptes Rendus, June 30, 1873.

tion of compounds is gradually evolved by the experimental study of the properties of the compounds, guided by certain general principles of the mechanics (143, note).

By *chemical constitution* of a compound, we mean the precise arrangement of the constituent atoms in any of the atoms of the compound, as expressed by the stereographic formula of the compound.

163. Numerically, this chemical constitution of a compound is expressed by the *table* of the *co-ordinates* of the constituent atoms in the compound atom.

Thus, the chemical constitution of ethane, C_2H_6, is, according to the stereographic formula of 158:

CO-ORDINATE.	TWO CARBON ATOMS.		SIX HYDROGEN ATOMS.					
x	0	1	—1	0	0	1	1	2
y	0	0	0	1	—1	1	—1	0
z	0	0	1	1	1	1	1	1

164. By means of our graphical formulæ, the subject of *isomerism* will become more clear. (See 148 and 149.)

Thus, the three isomers of the empirical formula $C_3H_6O_2$ described in 149 are represented in figure 5, namely:

A: Hydrogen propionate, $H\text{-}O\text{-}C_3H_5O$, a solid, boiling at 140°;

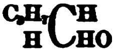
B: Methyl acetate, $CH_3\text{-}O\text{-}C_2H_3O$, a fragrant liquid, boiling at 56.3°; and,

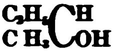
C: Ethyl formate, $C_2H_5\text{-}O\text{-}CHO$, a fragrant liquid, boiling at 54.9°.

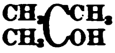
165. In figure 6 are represented five isomers of the empirical formula $C_4H_{10}O$, namely:

A: Ethyl-ether (common ether), $C_2H_5\text{-}O\text{-}C_2H_5$, boils at 34.5°;

B: Methyl-propyl-ether, $CH_3\text{-}O\text{-}C_3H_7$;

C: Butyl-alcohol, or propyl-carbinol,  ${}^{C_3H_7}_{\ \ H}C^{H}_{HO}$ boils at 115°;

D: Ethyl-methyl-carbinol,  ${}^{C_2H_5}_{CH_3}C^{H}_{OH}$ boils at 99°;

E: Trimethyl-carbinol,  ${}^{CH_3}_{CH_3}C^{CH_3}_{OH}$ boils at 82°.

These five compounds are so different in their physical properties (boiling point, etc.), and also in their chemical properties (reactions with KaH≐, etc.), that they cannot be mistaken one for another — and yet they have all exactly the same empirical formula.

166. We have shown how the boiling point of these isomers can be calculated from the graphical formula — so that *the physical and chemical facts of isomerism* are as *completely accounted for by the atomic theory here taught,* as the phenomena of double refraction and polarization are accounted for by the undulating theory of light. (See 340 to 354.)

167. Above all, it is important to bear in mind that *these phenomena of isomerism are the best possible evidence of the reality of chemical atoms,* and in themselves quite sufficient to establish the atomic theory as firmly as any other physical theory is established. (Compare 90; also, Induct. 5.)

168. It may not be improper to call special attention to these points, because so-called "philosophers" from time to time demolish all physical theories.* Such men are not scientists — not followers of Galileo, for they have no idea of *quantitative* induction—but they are mental descendants of that muddled thinker, Bacon, the grand master of all verbose speculators. (Compare Induct. 6.)

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* Thus, famous in his day, the great Prussian, Hegel, philosophically demonstrated the absurdity of the theory of universal gravitation; and now the great judge of Cincinnati, Stallo, demolishes (in Appleton's Popular Science Monthly) the atomic theory.

169. *Polymeric* compounds have the same percentage composition, but different molecular weight. If the smallest of these molecular weights, expressing the percentage composition, be called f, then the molecular weight of polymeric compounds will be n.f, where n is a whole number.

170. The *Olefines* constitute the most interesting *series* of polymeric compounds. They contain carbon and hydrogen in the proportion of 6 to 1 by weight; hence $f = CH_2$, and the general formula of the Olefines will be—

$$n.f = n(CH_2) = C_nH_{2n}.$$

The first two ($n = 2, 3$,) are gaseous at common temperatures; the next eight (namely, $n = 4, 5, 6, 7, 8, 9, 10, 15$,) are liquids; while the last two ($n = 27$ and 30) are solids.

171. We can now give a systematic enumeration of the principal serial compounds, corresponding to the simpler binaries and terniaries in Section VI.

172. A great many different systems of classification are possible, the field of serial compounds being so exceedingly rich, and the mutual connections between the different compounds so very numerous. One system would arise by taking up one radical after another, giving for each one all the compounds of importance it forms—as already exemplified in 126, 128, 129, 131, 132, for the serial monatomic alcohol radicals containing one and two carbon atoms. Each of these radicals thus is presented as the center of a vast number of compounds, and the radicals succeed one another from the simplest to the most complex. This system is very proper for larger, special treatises on organic chemistry.

173. For our purpose, it will be better to classify the compounds in a more general manner, according to their *type* and the *atomicity* of the radical. We shall consider, first, the *alcohol radicals;* next, the *aromatic radicals;* and, lastly, the *complex radicals.* These give, respectively, the alcohol serials, the aromatic serials, and the complex serials.

Section IX. Alcohol Serials.

174. *The alcohol serials* are (organic) compounds containing an alcohol radical. *Alcohol radicals* are derived from the paraffins (135, 136), especially by the removal of one or more atoms of hydrogen. The *atomicity* of the alcohol radicals is, in general, equal to the number of hydrogen atoms removed from the paraffin.

175. The general formula of the paraffins being C_nH_{2n+2}, the removal of m atoms of hydrogen will, in general, produce an m-atomic radical. The paraffins thus give rise to the organic radicals, comparable to the elements. The most important alcohol radicals have atomicities from *one* to *six.* We shall first consider the *monatomic* alcohol radicals; thereafter, all the others. In each group we shall enumerate the compounds in the order of the *types.* (See 150, 151.)

A. SERIALS OF MONOVALENT ALCOHOL RADICALS.

176. We will designate any monovalent alcohol radical by the symbols R and R′; so that either of these symbols may stand for methyl, ethyl, etc. (See 134, 135.)

When two atoms of hydrogen in methyl, CH_3, were replaced by their equivalent one atom of oxygen, the radical formyl, COH, resulted. Let, in general, *any* such *oxygenated* monovalent alcohol radical be represented by Ro and Ro′. In either case, the accent is used simply to indicate that the radical so marked is different from the one not marked.

177. It will be readily be seen that the *general formula* of the —

simple monovalent alcohol radical R is C_nH_{2n+1};
oxygenated " " " Ro " $C_nH_{2n-1}O$.

(Compare 175 and 176.) By means of these relations, the formulæ of the compounds given below can be written out in full, as soon as the value of n is given.

178. The following table enumerates the simple, R, and oxygenated, Ro, monatomic alcohol radicals:

n.	R.	Ro.
1	methyl	formyl
2	ethyl	acetyl
3	propyl	propionyl
4	butyl	butyryl
5	amyl	valeryl
6	hexyl	caproyl
7	heptyl	œnanthylyl
8	octyl	caprylyl
9	nonyl	pelargonyl
10	——	rutyl, or capryl
12	——	lauryl
14	——	myrystyl
16	cetyl	palmityl
18	——	stearyl
20	——	arachidyl
22	——	behemyl
27	ceryl	cerotyl
30	melissyl	melissyl

a. Hydrochloric Type, $\begin{matrix}H\\Cl\end{matrix}$.

179. The *hydride* of the simple radical is one of the paraffins, RH. Thus, amyl hydride is (n=5) $C_5H_{11}.H$.

The hydrides of the oxygenated radicals, RoH, are *aldehydes*. (See 185.)

180. The *haloid-ethers* are combinations of any simple monovalent alcohol radical with any of the choloroids (97). Formula, RX.

The common hydrochloric ether is really ethyl chloride; it is also called chlorethane. Give its formula; also that of bromethane, and iodethane.

Acid halides are combinations of any oxygenated monovalent alcohol radical with any of the chloroids; RoX.

Give the formula of acetyl chloride.

181. The *ketones* result from the combination of the simple and oxygenated monatomic radicals. General formula, RRo. But, since Ro may be considered as R′CO, this formula may also be written, R-CO-R′.

The most common ketone is *acetone*, or methyl-acetyl, CH_3-C_2H_3O. This formula may be written CH_3-CO-CH_3, according to which the compound is named di-methyl-ketone. Thus written, it is of the water type, wherein the diatomic oxygen is replaced by the diatomic carbonyl, CO.

Prove, by writing the general formulæ, that every ketone is isomeric with an aldehyde (179).

182. *Compound ethers*, or *ethereal salts* of monovalent acid radicals, belong here. Examples, for which write the formulæ:

Ethyl acetate; propyl propionate; ethyl nitrate, or common nitric ether; ethyl nitrite, or nitrous ether;* methyl nitrate; methyl acetate; amyl acetate; ethyl formate; methyl formate.

The compound ethers which contain a fatty acid (184) may be represented by R-O-Ro; they are often called *esters*. For example, methyl-acetate ester.

b. Water Type, $\begin{matrix}H\\H\end{matrix}O$, or H-O-H.

183. A (monatomic) *alcohol* is the combination of a simple monovalent alcohol radical with hydroxyl, HO. General formula, ROH, or $\begin{matrix}R\\H\end{matrix}O$.

Give the formula of methyl alcohol. (See 178.)

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* *Sweet spirits of nitre* of pharmacy are a solution of this ether, and of aldehyde in alcohol. It is obtained by the distillation of a mixture of twelve parts of alcohol with one part of nitric acid.

The following common names are in use for common commercial articles: n = 1, wood spirits; n = 2, alcohol, spirits of wine, aqua vitæ, proof spirit (containing 49.5 per cent by weight of real or *absolute alcohol*); n = 5, fusel oil.

184. A (monatomic) *acid* is the combination of an oxygenated monovalent alcohol radical with hydroxyl, OH. General formula, RoOH, or $\begin{matrix}Ro\\H\end{matrix}O$. These acids are also termed *fatty acids*, because n = 3 to 8 are *oily*, 9 to 30 *fatty*, in appearance.

The name of the acid is formed thus,

Ro-ic acid, or *hydrogen Ro-ate,*

when Ro stands for the *root* of the name of the oxygenated radical, obtained by dropping the ending *yl.* (See 178.)

Write the formulæ of: formic acid; hydrogen acetate; propionic acid; hydrogen lactate; stearic acid; hydrogen palmate.

The formula of the salts of these acids will be obtained according to the rules explained in 106 to 111. Thus, potassium stearate* is $C_{18}H_{35}O\text{-}O\text{-}Ka$.

185. By reduction, the fatty acids yield *aldehydes*, loosing the oxygen of the hydroxyl. Hence the general formula of monatomic aldehydes is RoH. (See 179.)

Give the formula of formic, acetic, propionic, butyric, valeric, and caproic aldehydes.

186. Ordinarily, aldehydes are prepared by the oxidation of the corresponding alcohol (by atmospheric air, or by dilute sulphuric acid and potassium bichromate). Thus, common alcohol gives, with O, acetic aldehyde and water; $C_2H_5OH + O$ gives $C_2H_3OH + H_2O$.

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* *Soft soaps* are impure potassium stearate, while *hard soaps* are impure sodium stearate, obtained bo the *saponification* of natural fats. Since these fats are mixtures of glycerine oleate, palmitate, and stearate, they yield, with potassium or sodium hydrate, a soap, as the result of double decomposition. Calcium stearate, etc., are insoluble; hence calcareous waters are *hard*.

The aldehydes are very readily changed to acid, by taking up one atom of oxygen. In this manner alcoholic liquids, when dilute and exposed to the influence of the air, acidify.*

187. The *anhydride* is the oxide of the oxygenated monovalent alcohol radical; Ro_2O. The most common is acetic anhydride, $(C_2H_3O)_2O$, which heavy liquid boils at 138°, and possesses a very pungent odor.

188. A *simple ether* is the oxide of a simple monovalent alcohol radical, R_2O, or $\left.\begin{matrix}R\\R\end{matrix}\right)O$. When the two simple radicals are different, containing a different number of carbon atoms, a *mixed* ether results, $\left.\begin{matrix}R\\R'\end{matrix}\right)O$.

Thus, common or sulphuric ether is really diethyl ether, $(C_2H_5)_2O$; it is very volatile, boiling at 34.5°. Methyl-ethyl ether, $(CH_3)\text{-}O\text{-}C_2H_5$, is a mixed ether, which boils at 11°.

Write the typical formulæ of: ethyl-amyl ether; butyl ether; amyl ether; ethyl-butyl ether; methyl ether.

189. Compound ethers, or ethereal salts of the water type, result from the combination of the alcohol radicals with diatomic acids. Thus, we have sulphovinic acid, $(C_2H_5)H\text{-}O_4S$, or hydric ethyl sulphate; also, diethyl sulphate, $(C_2H_5)_2O_4S$. (Compare 111.)

190. In figure 7 we have given the graphical formula of a few di-carbon compounds, in order to more fully elucidate the constitution of the different compounds above named.

a, ethyl hydride, gas; *b*, ethyl chloride, 12.5°; *c*, acetyl aldehyde, 22°; *d*, diethyl oxide, or ether, 34.5°; *e*, ethyl alcohol, 78°; *f*, diethyl ketone = ethyl propionyl, 101°; *g*, acetyl hydroxyl, or acetic acid, 120°; *h*, diacetyl oxide, or acetic anhydride, 138°. The boiling point has been added to the name.

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* Applied in the manufacture of vinegar, which is an impure and dilute aqueous solution of acetic acid. (Chem. 218.)

c. Ammonia Type, $\left.\begin{matrix}H\\H\end{matrix}\right\rangle N\,H$, or H_3N.

191. *Amines* are ammonias, wherein the hydrogen atoms are replaced by a simple monovalent alcohol radical, R. By the replacement of one, two, or three hydrogen atoms, result the —

primary	secondary	tertiary
$\left.\begin{matrix}R\\H\end{matrix}\right\rangle N\,H$	$\left.\begin{matrix}R\\R'\end{matrix}\right\rangle N\,H$	$\left.\begin{matrix}R\\R'\end{matrix}\right\rangle N\,R''$

amines. The radicals R′ and R″ may be different from one another, and from R.

Since these amines resemble ammonia, they are also often called *compound ammonias.* Thus, ethyl amine is ethyl ammonia, etc.

192. Write the full typical formulæ of the following amines, which boil at the temperature indicated after the *dash* (——), which stands for amine, to avoid the frequent repetition of this ending:

a. Primary amines: Methylamine, gas; ethyl——, 40.7°; propyl——, 49.7°; amyl——, 94°; hexyl——, 126°; heptyl——, 146°; octyl——, 170.

b. Secondary amines: Dimethylamine, 8.5°; methylethyl——; diethyl——, 57.5°; diamyl——, 170°.

c. Tertiary amines; Trimethylamine, 4° and 5; triethyl——, 91°; diethylamyl——, 154°; triamyl——, 257; methylethylamyl——, 135°.

193. *Amides* are ammonias, wherein the hydrogen is replaced by an oxygenated monovalent alcohol radical, Ro. They are primary, secondary, and tertiary, according as one, two, or all three of the hydrogen atoms in ammonia are replaced by the same or different oxygenated radicals.

Thus, we have acetamide, $\left.\begin{matrix}Ac\\H\end{matrix}\right\rangle N\,H$, which boils at 221°, and diacetamide, $\left.\begin{matrix}Ac\\Ac\end{matrix}\right\rangle N\,H$, wherein $Ac{=}C_2H_3O$ (see 132). Write the typical formulæ in full.

Alkalamides are ammonias containing both the simple and the oxygenated radicals, R and Ro.

Ethylacetamide is ${}^{Et}_{Ac}\mathrm{N}^{H}$; ethyldiacetamide, ${}^{Et}_{Ac}\mathrm{N}^{Ac}$ — of which write the typical formula in full.

194. *Carbamide*, $CO(NH_2)_2$, containing diatomic carbonyl, CO, is of especial interest; for it is *urea*, the waste product of organic tissue (Chem. 217), and the first organic compound artificially prepared (by Wöhler, 1828). Its formula is ${}^{H}_{H}\mathrm{N}\,CO\,\mathrm{N}^{H}_{H}$, represented graphically in Fig. 8.

Dry ammonia and carbon dioxide gases unite below 69°, by direct synthesis, to *ammonium carbamate.*

$$2\,NH_3 + CO_2 \text{ give } H_2N\text{-}CO\text{-}\overset{NH_4}{O}$$

and the latter, when heated to 130° to 140°, in a closed glass tube, loses one atom of water, and becomes urea.

195. When the nitrogen is replaced by phosphorus, we obtain *phosphines* from amines. In like manner, *arsines* result when nitrogen is replaced by arsenic, and *stibines* and *bismuthines* when replaced by antimony and bismuth.

Write the full typical formula of: trimethylarsine, 120°; triethylstibine, 158.5°; triethylbismuthine.

196. These compound ammonias deport themselves, in most respects, like ammonia, especially also in regard to acid radicals and hydroxyl, wherewith they form *alcoholic ammonium compounds.* These may, therefore, be considered as common ammonium compounds, wherein the above radicals replace the four atoms of hydrogen to any extent. (See 100.)

197. Now, by direct synthesis, ammonia, NH_3, and hydrogen chloride, HCl, give sal-ammoniac, or ammonium chloride, $NH_4Cl = AmCl$ (64). In the same manner, tertiary amines unite directly with haloid-ethers

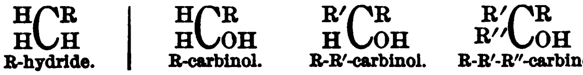
(180) to form the above alcoholic ammonium compounds. Thus, triethylamine, Et_3N, and ethyliodide, $EtIo$, unite to tetraethylammomium iodide, NEt_4Io. When the solution of this salt is treated with silver sulphate, we obtain AgI^{ide} and tetraethylammonium sulphate, $(NEt_4)_2O_4S$, exactly comparable to ammonium sulphate, $(NH_4)_2O_4S$.

As ammonium chloride gives a yellow crystalline precipitate of ammonium chloro-platinate, Am_2Cl_6Pt, with platinic chloride, $PtCl_4$, so will the alcoholic ammonium salts give corresponding chloro-platinates, as crystalline precipitates upon the addition of platinic chloride. Write the full formula of tetraethylammonium chloroplatinate. (See 116.)

d. Methane Type, ${}^{H}_{H}C^{H}_{H}$.

198. It is evident that this marsh-gas type will include nearly all the compounds enumerated in this section. Thus, one H replaced by R gives the hydrides of 179. By a chloroid substituted in the place of an additional hydrogen, the haloid-ethers of 180 result; while if hydroxyl, OH, takes the place of this second hydrogen, an alcohol will result (183); amidogen, H_2N, instead of hydroxyl, give an amine, etc., etc. But the types already given for these compounds are more convenient. We call attention to these new typical formulæ of the same compounds merely to confirm 152.

199. The great class of secondary and tertiary alcohols may, however, best be represented on this type. We have, accordingly, the following series:



${}^{H}_{H}C^{R}_{H}$	${}^{H}_{H}C^{R}_{OH}$	${}^{R'}_{H}C^{R}_{OH}$	${}^{R'}_{R''}C^{R}_{OH}$
R-hydride.	R-carbinol.	R-R′-carbinol.	R-R′-R″-carbinol.
or a	primary	secondary	tertiary alcohol.

Thus, carbinol ${}^{H}_{H}C^{H}_{OH}$ is methyl alcohol; methyl carbinol is ethyl alcohol, $R = CH_3$; etc.

Write, according to the above type, the full formula of: *a*, ethyl carbinol (or propyl alcohol); *b*, dimethyl carbinol (or isopropyl alcohol). Also the isomeric carbinols, $C_4H_{10}O$, namely: *c*, propyl carbinol (= butyl alcohol); *d*, isopropyl carbinol (= isoquartyl alcohol, 110°); *e*, methyl-ethyl carbinol, 95° to 98°; *f*, trimethyl carbinol. Fig. 9 represents these compounds.

The prefix *iso* to a radical, R, indicates that one extremity of the radical, R, has two CH_3 as termination, instead of one CH_3. (Compare 135 to 137). Thus, isopropyl is C_4H_9, or $C_2H_3(CH_3)_2$, or $-CH_2-CH-(CH_3)_2$, while propyl is C_4H_9, as $-CH_2-CH_2-CH_2-CH_3$.

200. The number of isomerics is very great in any of these series of compounds. Thus, the formula $C_6H_{15}N$ represents eight isomeric amines. Write their typical formulæ in full, and give the names of the same.

In this number of isomers, each alcohol radical is supposed to be without isomers; but merely the iso-modification of these radicals will increase this number to *fifteen* isomeric compounds of $C_6H_{15}N$. Give the formulæ and names. Thus far, these isomers have not yet all been experimentally obtained — but, if required, they undoubtedly will be prepared.

B. Serials of Polyvalent Alcohol Radicals.

201. From the paraffins may be obtained other than monovalent radicals. (Compare 175.) The *names* of these radicals are usually formed according to the following rule:

The paraffin (atomicity zero) has the ending *—ane*. The *monovalent* radical, resulting by the rempval of *one* hydrogen atom, has the suffix *—yl* instead (see table, 178). The *divalent* radical has the ending *—ene* (see 170); the trivalent gets the suffix *—enyl;* the *tetravalent* ends *—ine;* the *pentatomic*, *—inyl;* the *hexatomic*, *—one.*

Thus, we obtain from *propane*, C_3H_8, by successive removal of H: propyl, propene, propenyl, propine, propinyl, propone.

202. These radicals exhibit a great number of isomeric modifications. Thus, the most important tetravalent *ethine*, C_2H_2, commonly called *acetylene*,* is represented in Fig. 10, a; it combines with four atoms of chlorine in this modification. But in its most interesting compounds it is evidently *diatomic*, as represented in b. Finally, when in the free state, it is saturated, as indicated in c, where the one carbon should be supposed to have revolved around the axis drawn in the figure, so as to shorten the dotted line of the third bond (137).

Besides such isomerics, resulting from the different connections of the carbon atoms themselves, we have the usual isomerics, similar to those in 199.

203. Since now each of the isomeric radicals thus resulting from one empirical formula is the centre of a large group of compounds, it follows that the compounds of the polyvalent alcohol radicals are exceedingly numerous. It will, therefore, in these principles, be sufficient to refer to a few of the most prominent and important of these compounds.

204. In the construction of the formulæ, it must be borne in mind that diatomic radicals deport themselves like diatomic elements — that is, they combine with two atoms of chlorine, two atoms of hydroxyl, etc. (Compare 100.)

The *definitions* given in 176 to 200 for compounds of monovalent radicals remain in force, only changing the *number* of combining atoms in accordance with the atomicity, and prefixing this atomicity the *name*. Thus, a

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* Formed by synthesis when the voltaic arch (Phys. 446) passes between the carbon points in an atmosphere of hydrogen, By passing the gas through an ammoniacal solution of cuprous chloride, a red explosive precipitate, containing acetylene, is obtained, from which the gas is evolved in the pure state by means of hydrogen chloride.

diatomic alcohol is the combination of a simple divalent alcohol radical, R″, with two atoms of hydroxyl. Its formula is R″(OH)$_2$. (Compare 183).

205. *Ethylene*, C_2H_4 (Fig. 10, d), is the first radical of the diatomic series of alcohol compounds—it is also called olefiant gas, and heavy carburetted hydrogen. It is contained in common illuminating gas.

Ethylene alcohol, $C_2H_4(OH)_2$, is called *glycol*, and boils at 198°. (Fig. 10, e.)

All the diatomic alcohols aae termed *glycols*. Thus, propyl glycol is really propylene alcohol, $C_3H_6(OH)_2$. The typical formula of butyl glycol is $\left.\begin{matrix}C_4H_8\\H_2\end{matrix}\right\}O_2$.

Amylene, C_5H_{10}, has the constitution represented in Fig. 11, a. It is a very limpid liquid, boiling at 35°.

206. From these radicals result two different oxygenated radicals, giving rise to *two* series of diatomic acids. (See 184.)

In the *Lactic Acid Series*, the diatomic radical has substituted O for 2H; in the *Oxalic Acid Series*, 2O have taken the place of 4H in the same radical.

LACTIC ACID SERIES.		OXALIC ACID SERIES.	
Carbonic	H_2-O_2-C O		
Glycolic	H_2-O_2-C_2H_2O	Oxalic	H_2-O_2-C_2O_2
Lactic	H_2-O_2-C_3H_4O	Malonic	H_2-O_2-$C_3H_2O_2$
Butylactic	H_2-O_2-C_4H_6O	Succinic	H_2-O_2-$C_4H_4O_2$
Valerolactic	H_2-O_2-C_5H_8O	Pyrotartaric	H_2-O_2-$C_5H_6O_2$
Leucic	H_2-O_2-$C_6H_{10}O$	Adipic	H_2-O_2-$C_3H_8O_2$

The following two acids are also bibasic, or contain two atoms of replaceable hydrogen:

Malic acid	H_2-O_2-$C_4H_4O_3$
Tartaric acid	H_2-O_2-$C_4H_8O_4$

207. *Glycerine*, or *propenyl alcohol*, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$, is a triatomic alcohol, $C_3H_5(OH)_3$. Its specific gravity is 1.28;

has a sweet taste, and it is decomposed before it boils in air, but may be distilled in a current of steam. Fig. 10, f, represents its graphical formula.

When poured into concentrated nitric acid (or, better, in a cooled mixture of nitre and concentrated sulphuric acid), the three H are replaced by as many atoms of NO_2, giving the colorless, oily, poisonous liquid, *trinitrine*, commonly called *nitro-glycerine*, $\begin{matrix}C_3H_5\\(NO_2)_3\end{matrix}O_3$. (See Fig. 10, g.) When the atom is violently shaken, the two O will fall to the corresponding C, each one O will take 2H, and the nitrogen will be separated; or, from each atom of nitro-glycerine will result $3\,CO_2 + 2^1/_2 H_2O + 3\,N$, all gaseous, even the water, since the combination of C and O produces much heat. The graphical formula shows, therefore, very plainly that nitro-glycerine is exceedingly unstable, and since its decomposition yields gases, it is explosive (especially by percussion). The explosive *dynamite* is nitro-glycerine soaked up in porous siliceous powder. (See 390.)

208. Glycerine ethers (182) of higher fatty acids constitute *natural fats.* Thus, if stearyl, $C_{18}H_{35}O$, the radical of stearic acid (184), be represented by St, we have the ethers —

$\begin{matrix}C_3H_5\\StH_2\end{matrix}O_3$

Mono-Stearine.

$\begin{matrix}C_3H_5\\St_2H\end{matrix}O_3$

Di-Stearine.

$\begin{matrix}C_3H_5\\St_3\end{matrix}O_3$

Tri-Stearine.

Construct the graphical formula of tri-stearine.

The natural fats are mixtures of oleine, palmitine, and stearine, and yield their glycerine when treated with over-heated steam. (Compare 184.)

209. *Allyl* is isomeric with propenyl, but monatomic; consequently, *allyl alcohol* is $\begin{matrix}C_3H_5\\H\end{matrix}O$. (See Fig. 10, h, which compare to f.) The corresponding aldehyde is *acroleine*, $\begin{matrix}CH_3O\\H\end{matrix}$, which forms when glycerine or fats are incompletely burned, and possesses the well known penetrant odor produced by these combustions.

210. The tetratomic alcohol *erithrite*, ${}^{C_4H_6}_{H_4}O_4$, is a sugar-like solid, which occurs in certain lichens and fungi. *Citric acid*, $H_3(HO_7H_4C_6)$, is related to this alcohol.

Mannite, the chief constituent of *manna*, is a hexatomic alcohol, ${}^{C_6H_8}_{H_6}O_6$. (Fig. 10, k.) It crystallizes from its solution in alcohol. It is rather sweet, but not fermentable. *Dulcite* is isomeric with mannite.

The aldehyde of mannite is *dextrose*, ${}^{C_6H_7O}_{H_5}O_5$ (Fig. 10, l), one of the varieties of *glucose*. This brings us to the study of the great group of *saccharine bodies*, or *carbohydrates*. (Chem. 211.) But, as the exact constitution of these bodies is not sufficiently known, we shall treat of these in the section on Complex Serials. (See 238.)

C. HIGHER ALCOHOL RADICALS.

211. Besides the alcohol radicals referred to in the preceding section, a great many other hydrocarbons are known as radicals, each one of which is the center of a great group of serial compounds. These latter radicals contain relatively more of carbon, or less of hydrogen, than the alcohol radicals proper.

212. Thus, *terebene*, $C_{10}H_{16}$, a liquid which boils at 160°, results (indirectly) by the combination of two atoms of amylene, C_5H_{10}, under the separation of two atoms of hydrogen from each.

This synthesis is represented in Fig. 11, b; the resulting terebene in Fig. 11, c. For the constitution of amylene, see 205. The two pairs of hydrogen atoms enclosed by a bracket will unite to free molecules, and the carbon affinities so freed will combine.

*Caoutchouc** (*India rubber*) and *gutta percha* are polymers of C_5H_8. (Compare 169.)

213. Of the formula $C_{10}H_{16}$ several isomerics are

*** *Vulcanised rubber* is obtained by combining rubber with two to three per cent of sulphur. *Ebonite*, or *hard rubber*, also called *vulcanite*, contains more sulphur yet.**

known — the so-called *terpenes*. The most important of these are the *turpentine oils* of commerce. Many of the essential oils to which various vegetable matters owe their characteristic odor, are also largely composed of isomers of terebene. Other volatile oils may be considered products of oxidation of terpenes.

214. The *balsams* and *resins* of plants are similar oxygen derivations of these hydrocarbons. Common *camphor*, or laurel, has the empirical formula $C_{10}H_{16}$. Its constitution is not completely elucidated, but is intermediary between the terpene and true aromatic compounds.

Section X. Aromatic Serials.

215. The so-called aromatic compounds of organic chemistry rival the alcoholic compounds in number and in importance, both theoretical and practical. They are all referrable to *benzol*, which is itself a polymer (169) of acetylene (202) of the alcohol series.

We shall first indicate the principal hydrocarbons of the aromatic series, and thereafter select a few of the most important of the innumerable compounds derived from the same.

216. When acetylene, or ethine, C_2H_2, is exposed to a beginning red heat, its molecules combine to a molecule of *three* times its weight, giving *benzol*, C_6H_6. It is a saturated hydrocarbon (102, 103). It is a colorless liquid, $G = 0.8$, $t = 81°$; crystallizes at 0°.

The graphical formula of acetylene (Fig. 10, b,) of 202 shows that benzol has the graphical formula of Fig. 12, a, wherein the three dotted lines indicate the boundaries between the original acetylene atoms. To draw this formula readily, first draw the equilatrial triangle indicated in the figure.

This constitution of benzol is abundantly demonstrated by the reactions of the substance.

As suitable abbreviations, we can, in certain cases, use b or c (Fig. 12). The notation b is rapid, and most correct.

217. From benzol a number of higher saturated hydrocarbons have been obtained, each of which again is comparable to benzol. The principal of these are:

Napthaline, $C_{10}H_8$, Fig. 12, d; crystalline solid; fuses at 80°; boils at 218°, but distills at a lower temperature.

Anthracene, $C_{14}H_{10}$, Fig. 12, e; crystalline, fluorescent body; fuses at 213°; distills above 360°.

Pyrene, $C_{16}H_{10}$, Fig. 12, f; crystalline solid, which fuses at 142°.

Chrysene, $C_{18}H_{12}$, Fig. 12, g; crystallizes from its solution in benzol; fuses at 248°.

All of these aromatic hydrocarbons occur in *coal tar*, obtained by the dry distillation of bituminous coal. It also contains many of the hydrocarbons of the alcohol series.

218. By the substitution of hydrogen by alcohol radicals, new hydrocarbons result, the number of which is exceedingly great, on account of the great number of isomers that are possible.

To simplify the reference to the structure of the resulting compounds, it is customary to designate the places occupied by hydrogen atoms in benzol by the numbers 1 to 6, as exemplified in Fig. 13, a.

219. Thus, if two atoms of hydrogen are replaced by methyl, we shall have *three* isomeric *dimethyl benzols*, C_8H_{10}, or $C_6H_4(CH_3)_2$, according as the methyl atoms occupy the place 1 and 2 (Fig. 13, b), 1 and 3 (c), or 1 and 4 (d). It will be seen from this graphical formula (Fig. 12, a), that 3 and 4 or 5 and 6 give a compound identical with 1 and 2.

It is probable that the compounds designated by chemists as *ortho* compounds correspond to the positions 1 : 2; *meta* compounds to 1 : 3, and *para* compounds to 1 : 4.

Since C_8H_{10} is called *xylol*, we have for the above three isomers the following convenient names:

1:2 dimethylbenzol is called *orthoxylol;* it boils at 140°;
1:3 " " " " *metaxylol;* " " " 138°;
1:4 " " " " *paraxylol;* " " " 136°;
and solidifies to a crystalline mass at 15°.

220. *Trimethylbenzol*, C_9H_{12}, or $C_6H_3(CH_3)_3$—that is, benzol wherein three atoms of hydrogen have been replaced by methyl—gives, evidently, also three different isomers, namely: 1:2:3, 1:2:4, and 1:3:6, represented in Fig. 14, a, b, c. The last (c) is called *mesitylene*, which boils at 163°; b is *pseudocumol*, which boils at 166°.

Of course, the empirical formula, C_9H_{12}, also includes methyl-ethyl benzol, $C_6H_4(CH_3)(C_2H_5)$, of which, according to 219, there are three isomers (the only one known boils at 159°); and propylbenzol, $C_6H_5(C_3H_7)$, which boils at 157°; and isopropylbenzol, $C_6H_5[CH(CH_3)_2]$, which boils at 151°. The last two compounds are also called *cumols*.

Thus, we have already enumerated eight isomers C_9H_{12}. Construct the graphical formulæ of these eight isomers.

Since now each of these gives a series of compounds by substitution, etc., it will be apparent that the number of aromatic compounds is immense. We must, therefore, limit ourselves to the indication of a few prominent members of the same.

221. *Methylbenzol*, or benzol methyl, $C_6H_5(CH_3)$, is called *toluol*. It is a colorless liquid, G = 0.88, boils at 111°, and does not yet solidify at —20°. For its graphical formula, see Fig. 15, a. It gives rise to two isomeric series of compounds; for the exchange of hydrogen for any other monovalent radical may take place in the benzol radical itself, or in the methyl-radical appended.

The substitution products resulting from a substitution of the hydrogen of the methyl are called *benzyl* compounds, to distinguish them from those substitution products of toluol wherein only the benzol radical has been attacked, and which are called toluol compounds.

Thus, dichlortoluol is toluol wherein two atoms of chlorine occupy the places of an equal number of hydrogen atoms of the benzol radical; while the isomeric chlorbenzylchloride contains one atom of chlorine in the methyl, the other in the benzol radical.

222. The chlorine substitution products of toluol may serve as an example. For the sake of simplicity, let us adopt the formula m : n to designate that compound of this series, which contains m atoms of chlorine in the benzol radical and n atoms of chlorine in the methyl radical. Hence the compounds for which m + n has the same numerical value, are isomeric. Besides, for the same m : n several isomerics are possible, according to the place occupied by the m chlorine atoms.

223. In the following table, we give the observed boiling points. In a few cases, we add the observed fusing point in a bracket. The horizontal lines contain isomers.

m+n.	m : 0.	m : 1.	m : 2.	m : 3.
0	0 : 0, 111°.	—	—	—
1	1 : 0, 157°, para. 156°, ortho.	0 : 1, 176°.	—	—
2	2 : 0, 196°.	1 : 1, 214°.	0 : 2, 205°.	—
3	3 : 0, 235°, (76°)	2 : 1, 241°.	1 : 2, 234°, para. 229°, meta.	0 : 3, 214°.
4	4 : 0, 271°, (92°)	3 : 1, 273°.	2 : 2, 257°.	1 : 3 234°, ortho. 245°, para. 260, meta(30)
5	5 : 0, 301°, (218°)	4 : 1, 296°.	3 : 2, 281°.	2 : 3, 273°.
6	—	5 : 1, 326°, (103°)	4 : 2, 306°.	3 : 3, 308°, (82°)
7	—	—	5 : 2, 334°, (109°)	4 : 3, 316°, (104°)

For $m + n = 3$, five isomers are recorded in this table, and for the case of four chlorine atoms, the table contains six chlorides, the boiling points of which range from 235° to 273°.*

224. Benzol dissolves in concentrated nitric acid under evolution of heat. This solution can be exploded by means of a sudden shock (as nitro-glycerine — see 207). Upon the addition of water, the new compound formed separates as an oily, yellowish liquid, *nitro-benzol*, $C_6H_5(NO_2)$, which boils at 220°. It is evidently benzol, wherein one hydrogen is replaced by nitryl, NO_2.

225. In the reduction of this compound by the hydrogen evolved from zinc and sulphuric acid *in* the liquid, the oxygen of the nitryl is replaced by hydrogen, and *aniline*, $C_6H_5(NH_2)$, results (represented in Fig. 15, b). It is a colorless liquid, boiling at 181°; exposed to the air, it becomes brown. It combines with acids to salts, most of which crystallize readily.

Aniline and its salts are beautifully colored by the action of oxydizing agents. Thus, with chloride of lime (Chem. 178), they become first deep violet, thereafter dirty red. With concentrated sulphuric acid and potassium chromate, aniline turns blue — but this color also soon disappears.

226. The remarkable aniline colors are manufactured from *crude* aniline, which contains some *toluidine*, or amidotoluol — that is, aniline wherein one atom of hydrogen in the benzol is replaced by methyl. Its formula is $C_2H_4(NH_2)(CH_3)$; for its graphical formula, see Fig. 15, c — for the amidogen and methyl are diametrically opposite each other, in the places 1 and 4.

This *toluidine*, or *paramidotoluol*, is obtained from toluol, exactly as aniline results from benzol (224, 225). It crystallizes from dilute alcohol, fuses at 45°, and boils at 202°. It combines with acids to salts, and is an essential ingredient of crude aniline in the manufacture of aniline — for the removal of the methyl gives free points of attraction for the combination of the more complex coloring compounds.

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* As *examples* of the nomenclature in use, we quote: Tetrachlorbenzotrichloride (4:3); pentachlorbenzodichloride (5:2); pentachlortoluol (5:0). The numerical notation is, therefore, really called for.

227. Thus, *rosaniline*, $C_{20}H_{21}N_3$, is formed when crude aniline (containing toluidine) is heated in a closed vessel with arsenic acid. The resulting blackish red mass consists largely of rosaniline arsenate and arsenite, from which pure rosaniline is obtained by boiling with water, and precipitation by means of an alkali. The constitution of rosaniline is, according to Kekule's* view, represented by us graphically in Fig. 16. It will be seen that it consists of the essential parts of two toluidine and one aniline atoms.

The salts of rosaniline form greenish crystals of metallic lustre, and yield solutions of a beautiful red color. The common commercial salts are rosaniline acetate, sulphate, and hydrochloride.

228. *Phenols* are aromatic alcohols — that is, they result by the substitution of hydroxyl for hydrogen. (See 183.)

Phenol, or *carbolic acid*, is $C_6H_5(OH)$. It is a white, crystalline body, fusing at 35°, and boiling at 188°. It is a powerful antiseptic, and therefore extensively used as a disinfectant. It is extracted from the heavy coal tar oils.

Pyrogallol, or pyrogallic acid, is $C_6H_3(OH)_3$. It is obtained by exposing gallic acid to 200°. It reduces the precious metals from their solutions.

229. Phenol is strongly acted upon by concentrated nitric acid. According to the intensity of the action, one, two, or three atoms of hydrogen of the benzol are replaced by as many nitryl atoms, yielding mono-, di-, and finally *tri-nitrophenol.*

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* Berichte der D. Chem. Ges., 1871, p. 547.

The latter is also called *picric* (or *carbazotic*) *acid.* Its formula is evidently $C_6H_2(NO_2)_3(OH)$. It is a yellowish, crystalline solid, which fuses at 122.5°, and may be cautiously sublimated in small quantities—but in larger quantities it deflagrates upon heating. It is exceedingly bitter, difficultly soluble, but these solutions give to silk and wool a yellow color. Its salts (*picrates,* or *carbazotates*), are explosive—potassium picrate is used for blasting purposes.

230. *Benzyl alcohol* results from tuluol as phenol from benzol. It is C_6H_5-CH_2-HO. The corresponding *benzoic aldehyde* is an essential constituent of the oil of bitter almonds—it is C_6H_5-CO-H. *Benzoic acid* is C_6H_5-CO-OH, and occurs in many resins, especially in the gum benzoin, from which it is separated by sublimation.

231. Benzoic acid is specially interesting, because, in passing through the animal organism of man, it is converted into *hippuric acid,* $C_9H_9NO_3$, a compound which is always present in large proportion in the urine of herbivores. It has also been formed by direct synthesis. And, again, when hippuric acid solution is exposed to the atmosphere, it yields ammonia, glycolic acid (see 206), and benzoic acid (see 230).

232. Accordingly, the *constitution* of hippuric acid is established, both by synthesis and by decomposition, to be C_6H_5-CO-NH-CH_2CO-OH, as graphically represented in Fig. 17.

Show, in detail, by means of graphical formulæ, that the atom of hippuric acid, upon breaking up in its proximate constituents, will form, with the aid of two atoms of water, the above enumerated compounds, graphically represented at a, b, c, in Fig. 17.

We give this much detail about one single compound, because hippuric acid is admirably adapted to exemplify how the proximate constitution of even intricate compounds may be determined.

233. Several series of very peculiar *bases*, consisting of H, C, and N, and isomer with those of the aniline series, occur in coal tar. They may be considered as substitution products of the hydrocarbons, resulting by replacing one trivalent CH in the benzol radical by the trivalent N.

234. The *pyridine series* of bases starts from *pyridine*, C_5H_5N, Fig. 18, a, which compare to that of benzol (Fig. 12, a). By the addition of CH_2, result, successively, *piccoline*, *lutidine*, *collidine*, etc., to *viridine*, $C_{12}H_{19}N$.

235. The bases of the *chinoline series* are related to napthaline, exactly as the pyridine series is related to benzol. Fig. 8, b, probably represents the constitution of *chinoline*, C_9H_7N, which compare to Fig. 12, d. By the addition of CH_2, now follow *lepidine*, *dispoline*, etc., etc., up to *validine*, $C_{16}H_{21}N$.

This series of bases is obtained by the dry distillation of alkaloids, and thus will give some clue as to the constitution of these alkaloids. They do not occur in coal tar, which, however, contains three bases isomeric with with the first three of the above series.

Section XI. Complex Serials.

236. A great number of compounds occur in plants and animals—and their products of decomposition therefore occur in fossil state—the constitution of which has not yet been completely established. The great practical importance of these complex compounds, both in the economy of nature and in human industries, demands a short exposition of the principal groups of the same.

237. We shall roughly classify these compounds under three heads—as *carbonaceous*, *nitrogenous*, and *fossil complex serials*. In each of these groups, there is one natural group of bodies which, chemically, very closely resemble each other, and are also otherwise of paramount importance. These sub-groups are, respectively, the *amyloids*, *albuminoids*, and *paraffinoids*.

A. Carbonaceous Complex Serials.

238. The carbonaceous complex serials contain only carbon, hydrogen, and oxygen. The most common of these substances belong to the group of *amyloids*, which form the greater portion of all vegetable matter.

The amyloids are carbohydrates — that is, they correspond, empirically, to the formula $C_m(H_2O)_n$. (Compare Chem. 127.) They are also called *saccharine bodies*.

239. Their names and characteristic properties are given in the classified table printed on the next page, which see.

240. But a few remarks need here be added — since all necessary detail must be given in the lecture, or in the laboratory instructions.

The peculiar cellular form of starch and cellulose, different according to the plant from which they are derived, must be observed under the microscope. In the dark field of the polarizing microscope, the double refraction of these substances is then revealed by the beautiful colors which appear. (Phys. 290.) To obtain an alkaline cupric solution, add some potassium hydrate to the amyloid solution; to this add a few drops of cupric sulphate, which will not be precipitated, as it would be in the absence of the amyloid solution. Upon heating the blue liquid, the red precipitate of cuprous oxide, Cu_2O, will appear if the amyloid was a glucose or dextrine. The common glucose, also called *grape sugar*, is dextrose; sucrose is *cane sugar* (see Phys. 180, for form); lactose is *milk sugar*.

241. *Glucogene*, or *animal starch*, is intermediate between starch and gum. In its solubility it is a gum — but it is granular, and tinged (violet) by iodine, similar

GROUP:	SUCROSES.		GLUCOSES.		AMYLOSES.			
Formula:	$C_{12}(H_2O)_{11}$		$C_6(H_2O)_6$		$k\text{-}C_6(H_2O)_5$			
Name:	*Sucrose.*	*Lactose.*	*Dextrose.*	*Levulose.*	*Dextrine.*	*Gum.*	*Starch.*	*Cellulose.*
FORM.	CRYSTALLINE.			AMORPHOUS.			CELLULAR.	
	Perfect.		Imperfect.	Liquid.	Transparent Solid.		Granular.	Fibrous.
Dissolves in parts of *Water.*	$^1/_3$	6	$1^1/_3$	1	Very Soluble.		Insoluble.	
Dissolves in parts of *Alcohol.*	Less Soluble than in Water.				Insoluble in Alcohol.			
Alkaline Cupric Solution.	REDUCED TO CUPROUS OXIDE:					NOT REDUCED.		
	Slowly.	Cold.	Immediately, when heated.					
Special Characters.	Crystallize.		Ferment.		Mucous, Pasty.		Blue, by Iodine.	Dissolves in a solution of Cupric Oxide in Ammonia.
Optically:	Right-handed.			Left-handed	R't-handed.		Double Refracting.	

to starch. It is formed in the liver, and deposited in the muscular tissue, for use in muscular work. Oysters are rich in glucogene.

242. None of these compounds have yet been formed by synthesis; but they can all readily be converted into glucose.

Cellulose, when treated with strong hydrogen sulphate, will be tinged blue by iodine; hence it has been turned into the same modification of carbohydrate which we have in starch.

Boiling with dilute hydrogen sulphate, will change all other amyloids to glucose. Starch may also be so changed, by simply exposing the same to a temperature of 150° to 160° — especially if a very little of hydrogen chloride or nitrate has been added.

By the malting process — the artificial sprouting of barley — a peculiar ferment, *diastase* is formed, which also finally converts starch into glucose.

In the sprouting of seeds, starch changes to gum and glucoses, constituents of the sap. In the growth of the plant, these again revert to sugar, starch, cellulose.

243. *Glucose* is the only form of the amyloids which is fermentable; when any of the other forms appear to ferment, they have first changed to glucose.

The most common *fermentation* is *vinous*, or *alcoholic*, fermentation, which sets in spontaneously when grape juice is left exposed to the air, producing *wine*. This alcoholic fermentation is due to the vital process of minute cellular vegetation, the *torvula*, the oval cells of which are at most ten microns in longest diameter. In *brewer's yeast* they are exceedingly abundant. The groups of divergent strings of cells seen under the microscope are very beautiful.

244. Chemically, the resulting products of vinous fermentation are carbon dioxide gas and *alcohol* (Chem. 212), together with a small portion of a variety of other alcoholic, and a few aromatic, compounds.* The theoretical formula is—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} \text{ give } \underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}.$$

This fermentation occurs best at a temperature between 25° and 30°.

245. Other forms of fermentation are: acetous, lactic, butyric, and mucous fermentations—which processes also seem to be dependent on the growth of certain minute organisms. However, all the chemical products resulting can also be obtained direct, without any fermentation whatever. Thus, alcohol can be formed by the synthesis of ethylene, C_2H_4, and water, as will be explained in the next section. (See 294.)

246. Cellulose undergoes remarkable changes when treated with concentrated acids. Unsized paper, dipped for a few seconds in sulphuric acid (2 vols. acid to 1 vol. water), and then thoroughly washed with water and dilute ammonia, has not changed its composition, but its structure. It is now *parchment paper*, or *papyrin*—used for diplomas, etc., and considered by classical students to be "real" parchment.

247. When unsized paper (or any other form of cellulose) is dipped into a mixture of concentrated nitric and sulphuric acids, then squeezed, thoroughly washed, and gently dried, it has become *pyroxyline.* Formed from cotton, it is properly called *gun-cotton.* It is a substitution product of cellulose, three hydrogen atoms having (approximately) been replaced by nitryl, NO_2. Its formula is $k.C_6H_7(NO_2)_3O_5$, where, probably, $k = 3$. It is very explosive, and is used for blasting.

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* The strongest alcohol of commerce contains 85 per cent of alcohol. Proof spirit contains 50 per cent. Brandy, whisky, and other liquors contain 40 to 50 per cent. From the fermented liquids, alcohol may be distilled as follows: Strong wines (port, sherry), 20 to 10 per cent; light wines (claret and hock), 10 to 7 per cent; strong beers (ale, porter), 9 to 6 per cent; light beer (lager), 6 to 4 per cent.

Gun cutton is soluble in alcohol and ether — the solution is called *collodion.* This dries up rapidly, leaving a thin, air-tight film. Hence its use in surgery and photography.

248. *Glucosides* are vegetable products which yield glucose as one of the products of their decomposition. Such are tannine, salicine, and amygdaline.

Tannine, $C_{27}H_{22}O_{17}$, also called *tannic acid,* forms a black precipitate (ink) with ferric salts, and a thoroughly insoluble compound (leather) with gelatin. It occurs in the bark of plants, etc. When exposed to the air, it separates into three *gallic acid,* $C_7H_6O_5$, and one glucose. (Compare 228.)

249. *Salicine,* $C_{13}H_{18}O_7$, is the bitter principle of the pith of the willow and poplar. It crystallizes in beautiful double refracting needles from its solution in alcohol. It decomposes, by fermentation, into saligenine, $C_7H_8O_2$, and glucose.

250. *Amygdaline,* $C_{20}H_{27}NO_{11} + 2H_2O$, occurs in bitter almonds, which also, in separate cells, contain the ferment, synaptase, whereby the amygdaline is split up into hydride of benzoyl, C_7H_6O (see 230), hydrogen cyanide, $HCy = HCN$, and two atoms of glucose, with one of water. This fermentation necessarily takes place in the mastication of bitter almonds.

251. The products of decomposition thus obtained indicate, of course, the structure of the complex compound from which they result. Evidently, the glucose group in vegetable products is far from restricted to the amyloids. Its breaking up into alcohol, indicates that these compounds are related to alcohol in constitution. (Compare 231.)

B. NITROGENOUS COMPLEX SERIALS.

252. We shall here consider only the two principal groups of nitrogenous complex serials — namely, the *albuminoids* and the *alkaloids*. They contain, besides the three elements, C, H, O, also N as an essential constituent.

253. The *albuminoids* form the chief part of the solid constituents of the blood, muscles, glands, and many other organs of animals. They also occur, but rather sparingly, in many parts of plants, especially in the green portions, and in the seeds. Their atomic constitution is yet unknown; but they agree very closely in their percentage composition, which

	C	H	O	N	S	
averages—	54	7	22	16	1	per cent,
with a range of—	1	$^1/_5$	$1^1/_3$	$^1/_2$	$^1/_2$	per cent.

(Compare Chem. 217.)

254. The albuminoids are amorphous, more or less soluble in water, nearly insoluble in alcohol, and quite insoluble in ether. They are soluble in excess of acetic acid. In strong mineral acids, they dissolve upon partial decomposition — hydrogen chloride giving a solution which turns blue, and finally brown, while nitric acid gives a yellow solution. Caustic alkalies decompose the albuminoids — the products resulting vary according to the temperature at which the alkali acts.

255. *Egg albumin*, when dried at common temperature on glass plates, forms a yellow, transparent, gum-like mass. It does not re-dissolve in cold water, except upon the addition of a trace of free alkali; it is re-precipitated by acetic acid. Egg albumin *coagulates* when, in its original solution, it is heated to about 65°.

256. *Blood albumin.* or, more properly, *serum albumin*, is a similar body in the dry state; but it is readily re-dissolved in water, not precipitated by acetic acid, but readily by an excess of strong nitric acid. It is also precipitated from its solution by most of the salts of the heavy metals, and by alcohol. It begins to coagulate at about 60°, and has completely coagulated at 72°.

Serum albumin dissolves easily in strong nitric acid; egg albumin is almost insoluble in the same.

257. *Fibrin* is another albuminoid existing in solution in the blood; it solidifies immediately as the blood escapes from the body.[*] When freed from the corpuscles, it consists of whitish filaments, which are insoluble in water, and form a horny mass upon drying.

Myosin, the fibrinous substance of the muscles (flesh), resembles blood fibrin, but is not identic with the same.

258. *Casein* is the albuminoid of milk, from which it is separated upon the addition of an acid, the latter neutralizing the alkaline compounds to which the solution of casein was due. Cheese is this casein, together with more or less of butter and salts.

Protein, or potassium albuminate, which is, perhaps, $C_{72}H_{112}Ka_2N_{18}O_{20}S$, is obtained by the action of potassium hydrate, an egg albumin. It resembles casein in several respects.

259. The albuminoids of vegetables resemble the above. *Gluten* is the fibrin of wheaten flour, remaining after the starch has been washed out. *Legumin* is the vegetable casein, contained in peas and beans.

260. *Hæmoglobin* is the crystallizable, coloring albuminoid of the blood corpuscles — 87 per cent of the dried corpuscles is *hæmoglobin*, the balance being other colorless albuminoids. It crystallizes from defibrinated blood,[†] diluted by an equal volume of water, upon the addition of one-half a volume of strong alcohol and exposure to 0° or a still lower temperature.

261. Hæmoglobin, while closely agreeing in its percentage composition with the colorless albuminoids proper, differs from them all by being crystallizable, and by containing 0.4 per cent of iron as an essential ingredient. If this be taken as one atom, the empirical molecular formula (see 144) of hæmoglobin is (according to *Preyer*) Hb = $C_{600}H_{960}N_{154}FeS_3O_{177}$. Its molecular weight would therefore be 13332. We mention these *estimates* — for the formula is not accurately *determined* — as an instance of extreme complexity of the molecule.

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[*] If the blood flows from the artery immediately into a concentrated solution of sodium sulphate, the fibrin does not coagulate. This solution of fibrin may be decanted from the corpuscles, and precipitated by saturation with common salt.

[†] Especially that of dogs, cats, rats, mice, guinea pigs, many fishes, etc. From human blood the hæmoglobin has not yet been obtained in crystals.

Hæmatin, $C_{96}H_{102}N_{12}Fe_3O_{18}$, is a product of decomposition of hæmoglobin.

262. *Oxyhæmoglobin*, Hb-O_2, dissociates at common temperature, losing its oxygen. In veinous (dark) blood, the molecule of oxygen is partly replaced by carbon dioxide, giving reduced hæmoglobin, Hb-CO_2. In poisoning by carbonyl (carbonous oxide), this gas replaces the molecule of oxygen; but the carbonyl-hæmoglobin resulting is also bright red, Hb-CO.

In a like manner can the oxygen be replaced by other gases, such as H_2S, Cy, etc., which are poisonous.

263. Thus, the hæmoglobin — and consequently the blood corpuscles — are the carriers of the oxygen from the air to the most intimate parts of the system. They also carry the gaseous product of combustion out from the system. Each one of these little messengers is exceedingly minute, having a diameter of eight microns and a thickness of two microns in man; but they accomplish their great physiological task, since their number is so immense, each cubic millimeter of blood containing about five millions of corpuscles.

While the oxygen is almost exclusively combined with the hæmoglobin, the carbon dioxide is nearly equally divided between the corpuscles and the serum.

264. The chemical constitution (162) of the albuminoids is completely unknown. We only know that their proximate constituents must be related to the alcohol and aromatic serials, since the latter results when treated by oxidizers, acids, alkalies, heat, or even in the putrefaction which takes place when they are exposed to moisture and air at common temperatures. The compounds thus obtained usually contain not more than six carbon atoms.

265. *Gelatin* results when animal membranes, tendons, skin, and even bones, in part, are dissolved in water at higher temperatures; it is an animal jelly. By drying, it shrinks, and then constitutes *glue.*

The cortilage of ribs and joints give a similar substance, called *chondrin.*

Alum and lead acetate precipitate chondrin; they do not precipitate gelatin from its solutions.

266. Other nitrogenous animal substances, such as *keratin* (horny matter), *protagon* (nervous matter, also cerebrin), and others, will be found described in special treatises on animal chemistry.

The *bile* is especially rich in complex compounds, such as: *glycolic acid,* $C_{26}H_{43}NO_6$; *taurocholic acid,* $C_{26}H_{45}NSO_7$; *taurin,* $C_2H_7NSO_3$, which has been formed by direct synthesis; *cholic acid,* $C_{24}H_{40}O_5$, which may be recognized by Pettenkofer's test (Chem. 216.)

267. The *vegeto-alkaloids* are certain constituents of plants which act chemically as bases, and physiologically as powerful poisons (strychnine, etc.), and medicines (quinine, etc.) Some are liquid and volatile, and contain only C, H, and N; of these, conine has been obtained by chemical synthesis. Most are solid and non-volatile; they contain oxygen besides. In their chemical constition they resemble ammonia and ammonium compounds (191 to 197; also, 225). They produce, with platinic chloride, a chloroplatinate which is crystallizable — precisely as do the ammonium salts.

268. It may be sufficient here to give a tabular view of the composition of the principal alkaloids:

NAME OF ALKALOID.	BOILS	NUMBER OF ATOMS.					EXTRACTED FROM:
		C	H	N	O	H_2O	
Liquids:							
Piperidine..	106°	5	11	1	—	—	Black Pepper.
Conine......	212°	8	15	1	—	—	Hemlock.
Nicotine.....	240°	10	14	2	—	—	Tobacco, 2 to 8 ⅌ ct.
Solids:							
Morphine.........		17	19	1	3	1	Opium, the dried juice of the head of the poppy (papaver somniferum). Opium contains 10 to 15 ⅌ ct. of morphine.
Codeine............		18	21	1	3	1	
Thebaine..........		19	21	1	3	—	
Papaverine........		20	21	1	4	—	
Narcotine.........		22	23	1	7	—	
Narceine..........		23	29	1	9	—	
Strychnine		21	22	2	2	—	Strychnos nux vomica and Strychnos Ignatius.
Brucine		23	26	2	4	4	
Quinine............		20	24	2	2	—	Bark of Cinchona.
Cinchonine.......		20	24	2	1	—	
Cafeine, or Theine		8	10	2	2	1	Coffee, 1 ⅌ ct., Tea, 2 ⅌ ct.
Theobromine.....		7	8	2	2	—	Cocoa.

269. Of these alkaloids, only conine has, thus far, been obtained by synthesis; the others have been exclusively extracted from the vegetable substances named. Their salts, such as the chlorides and sulphates, are soluble in water; hence an acid solution, shaken with ether or chloroform, will give off fatty matters, etc., but not the alkaloid. But as they are deplaced from their aqueous solution by potassium or ammonium hydrate, and as they are soluble in ether or chloroform, an alkaline solution will, when shaken with ether or chloroform, yield the alkaloid to the ether or chloroform, from which it is usually obtained pure (and crystallized) upon the spontaneous volatilization of the solvent. (*Stas's Method.*)

270. Thus, strychnine is best extracted by first filtering an acid solution of the raw material, then adding potassium hydrate until slightly alkaline reaction, and shaking this solution with chloroform. The crystals may be identified by the exceedingly delicate color test described in Chem. 215, note.

Brucine gives a bright red to reddish brown color with concentrated nitric acid.

Quinine solutions, containing chlorine water, assume a green color, upon the addition of an excess of ammonium hydrate.

Morphine solutions assume a deep blue coloration upon the addition of neutral ferric chloride.

271. The most characteristic physiological action of the principal alkaloids is as follows:

Morphine diminishes the sensation of pain by its action on the nerves of sensation. Hence, in small doses, it produces sleep; in larger doses, it produces stupor, and finally death. Other opium alkaloids are more poisonous, and act differently. Thus, thebaine produces tetanus; hence it acts on the motor nerves.

Strychnine also acts on the motor nerves, producing violent tetanus. In small doses, it allays neuralgia.

Quinine is febrifuge, antiperiodic. It has been found that normal blood contains a peculiar fluorescent principle, and as quinine is strongly fluorescent, it probably restores that principle to the blood when miasmatic influences have diminished the amount thereof.

Cafeine (or theine) is a nervous stimulant, contained in the infusions of coffee and tea, universally used as beverages.

Woorara is arrow poison of South America. It resembles the alkaloids, acts on the terminations of the motor nerves in the striated muscles, so as to stop voluntary motion. It is completely and rapidly eliminated from the system by keeping up artificial respiration.

C. FOSSIL COMPLEX SERIALS.

272. In the rocks of the different formations are found *fossil complex serials*, resulting from the substance of plants and animals of past times. These serials are all combustible, and have been mineralogically described in Chem. pp. 154, 155. Here it may, therefore, be sufficient to indicate the products which are obtained in the *dry distillation* of coal, carried on for the purpose of manufacturing gas. The products thus obtained indicate, to a considerable extent, the constitution of these combustibles.

273. One gram of average gas coal gives 25 to 30 cgr of gas, tar, and ammoniacal water, and leaves a residue of 75 to 70 cgr of coke. The gas yielded occupies a volume of about 50 cc. Such a coal contains in each gram about 78 cgr carbon, 4 cgr hydrogen (total combustible, 82 cgr); also, of sulphur and nitrogen about 1 cgr, ashes 5 cgr; of water, chemically combined, 7 cgr; as hydroscopic or moisture, 5 cgr. But these proportions vary exceedingly. Thus, good Scotch cannel coal yields, per gram, 22 cgr of gas, 27 cgr of tar, 4 cgr of loss and ammoniacal water, leaving 47 cgr (or per cent) of coke.

274. The products resulting in the dry distillation of coal are: 1, *coke;* 2, *tar;* 3, *gas;* and, 4, *ammoniacal water*, also called *tar water*.

The coke remains in the *gas retorts*. The tar and tar water collect in the *condensers*. The gas gives off its most obnoxious *impurities* to the lime over which it has to pass on its way to the *gasometer*.

The proximate constituents of these different products is given in the following tables.

275. The *gas coke*, or *coke*, contains 90 to 93 per cent of corbon; the balance is ashes, containing some ferrous sulphide. Gas coke is a valuable fuel.

276. *Coal tar* separates by fractional distillation into *light tar oil*, *heavy tar oil*, and *artificial asphaltum*. These contain:

a. *Light Tar Oil*, consisting of *liquid* hydrocarbons......		aromatic...	Benzol,	art. 216
			Toluol,	" 221
			Xylol,	" 219
		alcoholic...	Propane,	" 136
			Quartane,	" 136
b. *Heavy Tar Oil.*	solid hydrocarbons....	aromatic...	Naphthaline,	art. 217
		alcoholic...	Paraffin,	" 135
	Acids....................		Carbolic,	" 228
	Bases....................		Pryidin, etc.,	" 234
			Chinoline, etc.	" 235

c. *Asphaltum.* Artificial asphaltum, with some free carbon.

277. *Coal gas*, or *illuminating gas*, contains *luminous* gases and vapors, *diluent* combustible, and therefore heating gases, and *impurities*, which either simply cool the flame (such as carbon dioxide, nitrogen), or give rise to noxious gases upon combustion (such as hydrogen sulphide, which gives sulphur dioxide).

a. *Luminous.*	*Gases* (alcoholic)		Ethylene,	C_2H_4
			Acetylene,	C_2H_2
			Tritylene,	C_3H_6
			Tetrylene,	C_4H_8
	Vapors	alcoholic	Propane,	C_3H_8
			Butane,	C_4H_{10}
		aromatic	Benzol,	C_6H_6
			Naphthaline,	$C_{10}H_8$
b. *Diluents:*	*Gases*................		Hydrogen,	HH
			Methane,	CH_4
			Carbonyl,	CO

c. *Impurities*............	cooling..	Carb'n dioxide,	CO_2
		Ammonia,	NH_3
		Nitrogen,	NN
	noxions..	Cyanogen,	CN
		H. Sulphide,	H_2S
		Sulphuretted Hydrocarbons.	

278. *Tar water*, or *ammoniacal water*, contains:

a. *Principal constituents*.........................	AmC^{ate}
	AmS^{ide}
b. *Accessory constituents*........................	$AmCl^{ide}$
	$AmCy^{ide}$
	$Am\ S\text{-}Cy^{ate}$

This tar water is now the source of the vast amount of ammonium compounds consumed.

279. *Petroleum* gives, upon fractional distillation, a similar series of paraffin products, except the so-called Rangoon tar, or Burmese naphtha, of India, which gives also a small amount of aromatic hydrocarbons.

The illuminating gases first passing off in the distillation of petroleum are but rarely used. Next follows the very volatile and limpid *rhigolene*, then *benzene*, *gasolene*, *kerosene*, etc. — all mixtures of gradually less volatile paraffins. (See 135.)

Safe kerosene should extinguish a burning match when dropped into the same, and not give an inflammable vapor until heated to 40° centigrade.

280. From this very imperfect sketch of the products of dry distillation of fossil combustibles, it appears that they really may be considered as complex serials, as was anticipated, on account of their origin. By careful gradual oxidation, it has been found that even anthracite and graphite have a very complex constitution, being molecular combinations of carbon. (Compare 77, and Chem. pp. 154, 129.)

Section XII. Synthesis of Serials.

281. The serials mentioned in the preceding five sections (VII. to XI.) are also termed *organic compounds*, because they were formerly derived from animal or vegetable materials. It was then thought that such organic compounds could only be obtained from the mineral compounds through the action of *life*, either in plants or in animals. Many eminent chemists were led by a false philosophy to the belief that organic compounds would never be obtained by chemical reactions in the laboratory, because they thought the plants and animals in possession of a special, occult *vital force*, different from the known physical forces.

282. But it is well understood now that no such special force does exist. The energy exerted by animals is due to physical causes. Nothing is created by them — they simply set free a portion of the force which is latent (potential) in the food they consume (Chem. 84.) In a like manner, plants have no power, except that which they obtain from the sun and their food. (See Cosmos.) Hence, the philosophy which is based exclusively on a careful observation of natural phenomena, cannot countenance the idea that the chemical products which constitute the body of plants and animals have been formed under the influence of any force other than those inherent to ordinary matter not yet part of any living being.

283. In other words, any compound which occurs in plants or animals will, some day, also be formed in the laboratory, by means of the elements and the ordinary physical agencies. But, since the organic compounds are often quite complex, and since the amount of force brought to play is relatively very small, it is not to be wondered that for some time organic synthesis appeared impossible.

284. In 1828, *Woehler* obtained urea by simple chemical processes (see **194**), and theredy proved that organic synthesis was possible. But as this is, in some sense, a waste product of animal life, the speculative philosophers continued their assertions. Even after *Kolbe* had, in 1845, built up acetic acid from carbon bisulphide — and thereby, indirectly, a vast number of alcoholic compounds — the impossibility of forming, chemically, by simple synthesis, organic compounds continued to be asserted.

285. To-day, the number of organic compounds which have been built up, by continuous synthesis, from the inorganic elements, by the application of simple physical agents in the laboratory, has become so vast that, to all minds not biased by philosophical doctrines, the actual synthesis of *any* organic compound is simply considered a question of time.

286. Only the so-called complex serials have, thus far, not yet been obtained by synthesis; but a great many facts, indicating their proximate constitution, have already been obtained by the study of their gradual oxidation and decomposition. In the past, this knowledge has always led to a successful synthesis — and there is no reason why it should be different for the future.

We therefore consider the synthesis of albuminoids, amyloids, etc., as possible.* Whether any of these substances will ever be made economically, so that the manufactured product can compete with the natural, is quite another question.

287. But all the urea now in the market is manufactured in the laboratory, and not extracted from animal refuse matters. The manufacture of artificial *alizarin* is just now beginning to drive the natural alizarin (*madder*) from the market — thereby relieving vast districts of territory from madder culture, so that they can be devoted to the growth of cereals for food.* Since madder is a very complex coloring compound, this synthesis is doubly interesting, and quite decisive. Indigo will undoubtedly soon also be manufactured in chemical laboratories.

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* This does not imply anything in regard to the *structure* which some of these substances possess. Thus, the material *cellulose* may be made, although no *cell* structure be formed. The question of structure belongs to biology, not to chemistry.—*Darwin.*

288. By the following course of reactions, alizarin is built up from the simple elements:

Carbon and *hydrogen* unite directly to *acetylene* (see 202); this is condensed to *benzol* (see 216) and *anthracene* (217). Anthracene, $C_{14}H_{10}$, is oxidized, by means of nitric or chromic acid, to *anthraquinone*, $C_{14}H_8O_2$. When this is treated at about 260° with concentrated sulphuric acid, there results *disulphoanthraquinone*, $C_{14}H_6(HO_3S)_2O_2$. The excess of sulphuric acid is precipitated by lime, as gypsum; whereby, at the same time, the calciumsalt of anthraquinone is formed. The addition of sodium carbonate now gives the sodium salt, $C_{14}H_6(SO_3Na)_2O_2$, from which the precipitated calcium carbonate is removed. The soda salt is then heated to about 180° with sodium hydrate, giving the sodium salt of alizarin as a beautiful violet solution and sodium sulphite. Sulphuric acid finally precipitates the *alizarin*, $C_{14}H_6(OH)_2O_2$, as an orange-yellow powder.

In the manufacture, anthracene is obtained from coal tar, which contains about one per cent thereof.

289. It deserves a very special mention, that this artificial formation of alizarin has resulted from a very careful study of the rational formulæ of certain allied compounds. This proves that the determination of the rational formulæ is not only of the highest possible chemical importance, but also of great economic value—at least it has proved so in this case,* and in many others.

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* In Lancashire alone, one hundred and fifty tons of madder were used weekly, and, as an acre yields only one to two thousand pounds of the dried roots, about twenty thousand acres are required to yield the product for one week, or a million acres of madder are to be cultivated to furnish the material for Lancashire alone. But the plant requires one and a half to three years before its root is fit for use — so that the above one hundred and fifty tons of madder per week really necessitates the cultivatton of about two million of acres.

The synthesis of alizarin was effected by Græbe and Liebermann only a few years ago, and now large manufactories in Germany and England produce the precious color chemically in immense quantities.

290. The preceding notes may suffice to give an idea of the work and importance of organic synthesis in general. For a full synopsis of the subject, we must refer to special treatises of *Berthelot*, who has added so largely to those methods of synthesis whereby the organic compounds can be obtained directly from the inorganic elements. His "Chimie Organique fondée sur la Synthèse," published in 1860, is out of print; but his excellent "Traité Elémentaire de Chimie Organique,"—Paris, 1872,—gives sufficient of details.

291. We shall here give a few of the most instructive examples of the synthesis of organic compounds, after *Berthelot.*

The starting point is the synthesis of acetylene, C_2H_2 (see 202), for the other simple compounds constantly used in the processes of organic synthesis have long been obtained by simple synthesis from inorganic materials—namely, the compounds CO, CO_2, H_2O, H_3N, and a few others.

292. The synthesis of common (ethyl) alcohol involves the synthesis of the innumerable compounds derived from the same—a few of which are indicated in 131, 132, 133. Really, it involves the synthesis of a large portion of the alcohol serials, since it is possible to pass from the lower members to the higher members by various means.

293. One method of forming the higher compounds of the alcohol series by means of the lower ones (*i. e.*, containing less of carbon), consists in the addition of carbonyl to an alcohol. This can be effected by various means,[*] and gives an acid containing one more carbon atom than the alcohol. From this acid the corresponding alcohol is obtained by reduction (185). This alcohol gives, thereafter, again the next higher acid, etc. In this way, the addition of CO and the subsequent reduction gives constantly higher and higher monatomic alcohols. As now each of these is the center for a vast group of derived compounds, it is evident that the formation of any alcohol from the elements involves the synthesis of a great majority of the alcoholic serials.

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* See W. J. Russell, in Nature, September 18, 1873, pp. 416—419.

Fig. 19 represents this series of reactions in a general way — the upper row, A, exhibiting the carbonyl atoms gradually added to the alcohols in line B, thereby producing the acids of line C, which again, by the hydrogen indicated in line D, are reduced to their alcohols. It is recommended to write out the corresponding formulæ and the chemical equations representing these processes. The numerals indicate the number of carbon atoms contained in the alcohols and acids. The arrow-heads in line A indicate the water given off in the reduction of the acid to alcohol.

294. The synthesis of ethyl alcohol, C_2H_5OH, is effected by *Berthelot* in this manner:

Carbon and hydrogen unite to acetylene, C_2H_2 (202), which takes up, by direct synthesis, gaseous hydrogen to form ethylene, C_2H_4 (205). This gas[†] is absorbed by strong sulphuric acid, especially upon shaking, forming sulphovinic acid, $C_2H_4\text{-}H_2O_4S$. When this is diluted and distilled, alcohol, $C_2H_4\text{-}H_2O$, passes off, water taking the place of the hydrogen sulphate.

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[*] The carbonyl, CO, may be added in the shape of carbonyl chloride, $COCl_2$, commonly called phosphene gas, to the paraffin, giving HCl and the acid chloride. Thus, $CH_4 + COCl_2$ give $HCl + C_2H_3OCl$ (acetyl chloride). The addition of water gives the acid, hydroxyl taking the place of chlorine—under separation of HCl.

[†] Hence, alcohol can be manufactured from the ethylene contained in common illuminating gas.

From this alcohol the higher alcohol compounds are obtained, as shown before (293).

Fig. 20 represents the synthesis of alcohol and the synthesis of sulphuric acid (Chem. 135), showing the "organic" synthesis to be quite parallel to the "inorganic" synthesis, as asserted before (285).

295. The lowest alcohol, methyl alcohol, results from methane, CH_4, in various ways;* and this marsh gas forms always under the regeneration of acetylene, when ethene is exposed to a red heat in the presence of hydrogen — namely:

$$\underset{\text{Ethene.}}{2\,C_2H_4} + H_2 \text{ give } \underset{\text{Methane.}}{2\,CH_4} + \underset{\text{Acetylene}}{C_2H_2}.$$

Having the alcohol, of course all the other compounds of methyl (126) and formyl (129) are obtained in the usual manner.

296. Since the heating of acetylene produces benzol, and other aromatic hydrocarbons (216, 217), the synthesis of the aromatic serials has also been very largely effected. One of the most striking examples of this kind is the synthesis of alizarin, referred to in 288.

297. Thus, there remain only the complex serials as compounds so far not obtained by synthesis from the elements. But in this case we have already made the first step required for such a synthesis — the products of decomposition have been studied, indicating more or less completely the chemical constitution of these compounds — so that the successful synthesis appears to be only a question of time. For example: Woody fibre can be changed to water and *glucose* (242), which latter yields carbon dioxide and alcohol, constituents formed by synthesis. It remains to form glucose of carbon dioxide and alcohol, and to unite the glucose and water to woody fibre. Although this synthesis has not yet been effected to-day, it may be an easy thing to-morrow.

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* Methane mixed with chlorine gives methyl chloride when the mixture is exposed to direct sunlight. When this chloride is distilled with potassium hydrate, methyl alcohol passes over.

298. When alcohol is burned, each atom, C_2H_6O, combines with six atoms of oxyen, and yields two atoms of carbon dioxide and three atoms of water as products of complete combustion. At low temperatures, the combustion of alcohol — and of any other complex compound — takes place gradually. This process of *gradual oxidation* being so important in the phenomena of life and decay of animals and plants, we shall here give the series of products the successive stages yielded by the gradual oxidation of alcohol. The student should write out the formulæ in full, and the chemical equations according to Fig. 21, wherein A represents an atom of alcohol; B, aldehyde; C, acetic acid; D, oxalic acid; E, formic acid; F, carbonyl. Each atom of oxygen added is represented by a small circle, while each atom of water separated is indicated by a single arrow-head, and each atom of carbon dioxide by a double arrow-head. Write out such a chart, with full rational formulæ.

299. The few examples of organic synthesis may properly be supplemented by a reference to *Berthelot's* general method of reduction by means of hydrogen iodide. When any serial compound is enclosed with a proper amount of hydrogen iodide in a strong glass tube, and heated to a proper temperature for a sufficient length of time, it is completely hydrogenized — *i. e*, the corresponding saturated hydrocarbon from which the compound might have been derived (134) is regenerated. Thus, if alcohol is so treated, ethane will be produced.

300. Accordingly, we may indeed look upon the paraffins as the serial elements, and acetylene as the primary organic matter from which they can be derived. By synthesis, gradually more and more complex compounds have been built up. By gradual oxidation they can be completely oxidized, and by hydrogenation the original paraffin can be regenerated. There is, consequently, no valid reason to set organic compounds apart as distinct from inorganic compounds, due to the influence of some occult "vital force." That certain complex serials have not yet been formed by synthesis, cannot be used as a reason for such distinction—since there are many minerals which, so far, have not been obtained by synthesis either. Are we, perchance, to ascribe the formation of certain complex silicates to a vital force of the rocks? Neither can modern chemists ascribe the formation of complex compounds in animals and plants to a vital force peculiar to life.

Section XIII. Molecular Rotations.

301. According to the modern mechanical theory of gases, the molecules move freely, in straight lines, and with uniform velocity, until they impinge against one another, or against the walls of the containing vessel. (See 42, c to g.) Then they rebound as equal elastic bodies, retaining the same velocity, but having changed the direction of their motion.

302. But the molecules are *not* spherical, as a glance at the graphical formulæ represented on Plate I. will show. Hence, the impact will not only produce a *motion of translation*, but also a *motion of rotation of the molecules.* (Hinrichs, 1872.)

As the impacts succeed one another with great rapidity, and in all conceivable manners, the molecules will assume that motion of rotation which is the most stable.*

303. In dynamics, it is demonstrated that a body, unsupported and in motion through space (motion of translation), has but one axis of most stable rotation—

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* It is not necessary in these elementary principles to refer to the resultant motion as function of the individual motions, determined by the law of probability. (Induct. 84.) See Section XV. of this volume for an example.

namely, the *natural** *axis*, for which the momentum of inertia of the body is *maximum*. (See 312.)

If the body is nearly uniform in material, the natural axis is perpendicular to the plane of greatest extension of the body. (Compare Induct. 72.)

304. These two motions of an unsupported (*i. e.*, *free*) body may be exhibited by means of a card-paper *boomerang* (Fig. 22), 9 cm long, 1 cm wide, the two arms forming an angle, abc, of one hundred to one hundred and ten degrees, while the plane of the paper should be bent about five degrees at the elbow, b. Such a boomerang weighs only about half a gram. It is put in motion by striking a quick blow with the flat side of an elastic paper-cutter, d, in the direction of the arrow, while the boomerang rests upon the smooth surface of a body, AB (best of glass), held in the left hand at about the height of the chin.

305. The blow will give the boomerang a rapid motion; but as the blow was excentric (*i. e.*, not directed through the center of gravity, O, of the boomerang), it will also produce a rapid rotary motion around the natural axis of maximum moment of inertia (*i. e.*, vertical in O). So far, the case is exactly parallel to the motion of a molecule of any gas, according to 302. But the boomerang being screw-like, and moving in a resisting medium, will, furthermore, *return* to the point from which it was projected — while the molecules continue their motion of translation until they impinge against any obstacle.

306. It will be seen that the natural axis in the direction of a O c has a minimum moment of inertia, while the natural axis, O b, is intermediate between the maximal axis, perpendicular to O, and the minimal axis, a O c.

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* A *natural* axis is an axis of rotation which passes through the center of gravity, and for which the moment of inertia of the body is either greatest, least, or at right angles to both of these axes. Hence, each body has *three* natural axes.

This may be exemplified by means of a boomerang twice as large as the above, and made of wood. When suspended to the axis of rotation of a centrifugal machine by a string attached to c, it will rotate around this minimal axis so long as the rotation is sufficiently slow; but as soon as the rotation attains a certain degree of rapidity, the plate will lift itself aud rotate around its maximal axis.

By simply attaching this boomerang to a thin catgut string, about half a meter long, and turning the upper end of this string rapidly between the thumb and first finger, the two hands rapidly alternating, so as to produce a continuous rotation, the same phenomena may be exhibited without the aid of a centrifugal machine. (Compare Induct. 72.)

307. These well known principles of dynamics I have, since 1872, mathematically applied to the *dynamics of chemical molecules.* Thereby the obscurity which has long rested upon the *three states of aggregation* has been removed, and a number of very important and general laws of *thermodynamics* have been established. For the details, I must refer to the original papers, and to my *Molecular Mechanics*, which has been in the course of preparation for many years.

308. The following definitions appear to express the molecular motions in the three states of aggregation:

1. *The molecules of a body in the* GASEOUS *condition have a motion of translation* (42, e), *and* ALSO A MOTION OF ROTATION AROUND THEIR NATURAL AXIS OF MAXIMUM MOMENT OF INERTIA.

2. *The molecules of a body when in the solid state have only a vibratory motion about a position of equilibrium.*

3. *The molecules of a body when in the liquid state have a vibratory motion, as in the solid state, and* ALSO A MOTION OF ROTATION AROUND THEIR NATURAL AXIS OF MINIMUM MOMENT OF INERTIA.

These rotary motions of the molecules were first recognized and demonstrated by the author.

309. We can now understand the *changes of the state of aggregation by heat.* (Chem., Chap. I., Sec. IV., and Chem. 86 to 88.)

Since the absolute temperature of a body really expresses the actual enery or *vis viva* of its molecules (42, c, and Induct. 59), it is evident that an increase in the temperature of the solid will first increase the rapidity and excursion of the vibrating molecules. At a certain point, these vibrations will be associated with rotations around the natural axis of least momentum, while finally, when the continually increasing temperature has reached another fixed point, the molecules will fly freely into space, and revolve around their natural axis of greatest momentum. If now the temperature be lowered — *i. e.*, the actual energy of motion diminished — the motions of the molecules change in the opposite order.

310. By means of the experiments of 306, these changes of the states of aggregation may be illustrated. The body should first oscillate like a pendulum, and then be subjected to an increasing rapidity of rotation around its longest axis. It will then represent, in succession, a molecule of a body in the solid, in the liquid, and in the gaseous state of aggregation. Upon ceasing to rotate, the body will gradually come to rest, and thus exhibit the motions of a molecule of a body in the gaseous, the liquid, and the solid states. The final rest corresponds, of course, to the molecule of a body of a temperature of absolute zero, or —273° C. (See 42, d.)

311. We believe to have established an additional and very remarkable instance of *unity in nature* — for, obviously, the motions of the cosmical bodies in the celestial space correspond exactly to the motions of a molecule in a gas. In both cases, the body has a free motion of translation associated with a motion of rotation around an axis which passes through the center of gravity of the body, and for which the moment of inertia of the body is a maximum.

After these general explanations of this subject of molecular rototions, we shall show how the moment of inertia of molecules can be determined, and how these values can be experimentally verified.

312. *The moment of inertia,* I, *of any given body in regard to any given axis of rotation is the sum,* Σ, *of the products,* $m . x^2$, *of each component mass,* m, *into the square of its distance,* x, *from the given axis of rotation.* (See Induct. 67.)

$$I = \Sigma\, m . x^2.$$

If, therefore, these distances, x, and masses, m, are known, the moment of inertia will easily be obtained. The mass of a hydrogen atom is taken as unity, so that m is represented by the same numbers which represent the atomic weights. (See 18.)

For the general method, see the author's note in *Comptes Rendus,* June 30, 1873.

313. *The radius of gyration,* R, is the distance from the axis to that point at which the entire mass, M, would have to be, in order to give the same moment of inertia, I, as the actual body. Consequently,

$$I = M . R^2;$$

by which equation R may be calculated if M and I are known.

Thus, the mass of dimethyldiethylmethane being $M = 100$, and the maximal moment of inertia being $I = 178$, the radius of gyration for the same maximal axis will be $R = \sqrt{1.78} = 1.335$.

314. The moment of inertia of dimethyldiethylmethane, $\overset{CH_3}{\underset{C_2H_5}{}}C\overset{CH_3}{\underset{C_2H_5}{}}$, for its three natural axes can easily be calculated by use of the above mechanical definition.

The graphical formula is represented at A in Fig. 23. In order that we may readily refer to each part, we have represented the same compound by letters at B in the same figure. Hence, a, e, f, g represent $CH_3 = 15$; b and d represent $CH_2 = 14$; and $c = C = 12$. Also, the distances $ab = bc = cd = de = cf = cg =$ unity.

Since c is evidently the center of gravity, we have:

1. The maximal moment of inertia, I, for the natural axis at right angles to the plane of the figure at c—

$$I = a.2^2 + b.1^2 + c.0^2 + d.1^2 + e.2^2 + f.1^2 + g.1^2 = 178.$$

2. The intermediate moment of inertia, j, for the natural axis fg—

$$j = (a+e)\,2^2 + (b+d)\,1^2 + (f+c+g)\,0^2 = 148.$$

3. The minimal moment of inertia, i, for the natural axis ae—

$$i = (a+b+c+d+e)\,0^2 + (f+g)\,1^2 = 30.$$

Accordingly, the dimethyldiethylmethane atoms rotate around the natural maximal axis c of moment of inertia, $I = 178$, when the substance is gaseous, but around the natural minimal axis ae of moment of inertia, $i = 30$, when the substance is liquid.

Demonstrate that the maximal moment of inertia of heptane is 410; pentane, 148; tetramethylmethane, 60.

315. The *molecular volume* of a liquid is, according to our definition of the liquid state (308), evidently proportional to the length of the greatest natural axis and the square of the intermediate axis; for the cylinder described by the atom rotating about ae (Fig. 23) is evidently proportional to ae times $(fg)^2$.

316. For all liquid compounds, the molecules of which have the same cross-section, the molecular volume is evidently proportional to the *length* of the atom.

If n be the number of carbon atoms in this line, then Fig. 23, c, shows that *the length of the molecule* is $n + 1$, if each hydrogen atom occupies half as great a space as the carbon atom. By comparison, it may be inferred that the unit of volume is that of a molecule of water.

Accordingly, the molecular volume of the common carbon serials of equal cross-section will be $n+1$, when liquid, the molecular volume of water being taken as unity.

317. The *molecular volume*, v, occupied by one milligram-molecule, a, is evidently —

$$v = \frac{a}{s} \text{ cubic millimeters,}$$

if s is the specific gravity of the substance.

Hence, the milligram-molecule volume of water is 18 cubic millimeters. If we take the volume of a milligram-molecule of water as unity, then the molecular volume of any substance will be —

$$v' = \frac{a}{18.s}$$

where a and s have the same signification as above.

By these formulæ, the molecular volume of compounds is experimentally determined by the determination of the specific gravity of the substance. Hence, the law of 316 can be tested by experiment.

318. The law of 316 was first published by us in 1868. We copy the following table of acids from the paper referred to.* Here n is the number of carbon atoms; s, the specific gravity; v′, the atomic or molecular volume, that of water being unity; v″ is the theoretical volume, $1+n$; d, the error in per cent of this latter; and, finally, t is the boiling point:

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* Report of the seventeenth meeting of the American Association for the Advancement of Science, held in Chicago, in 1868. For some serial compounds, Prof. Hunt had already referred the molecular volume to that of water.

ACID.	n.	s.	v′.	v″.	d.	t.
Formic......	1	1.235	2.07	2.00	+3	100
Acetic........	2	1.063	3.12	3.00	+4	118
Propionic....	3	0.991	4.12	4.00	+3	140
Butyric......	4	0.974	5.015	5.00	+0.3	162
Valerianic...	5	0.938	6.030	6.00	+0.5	174
Caproic......	6	0.931	6.916	7.00	—1.4	199
Lauric.......	12	0.883	12.604	13.00	—3.2	?

319. The regular diminution of the differences, d, indicates that for corresponding temperatures—*i. e.*, for temperatures at equal distance from the boiling point—these differences would disappear.

320. It cannot be denied that this law is not very accurately and fully established. In fact, the rotations around the longer axis, for which the momentum of inertia is a minimum, are most difficultly determined, because the proximity of the molecules in the liquid state is a disturbing cause. But in the gaseous state, the molecules moving freely at distances averaging more than ten times the molecular distance in the liquid state, the internal work must be nearly zero; and hence the molecular rotation around the maximal natural axis must be more easily demonstrated.

Such being the fact, the specific heat of vapors, and the boiling points of isomers, most firmly establish this molecular rotation.

321. The specific heat of vapors is a much less complex quantity than that of solids or liquids (see 78); but still it is not very simple. The following exposition will show this, and at the same time lead to a most important demonstration of the rotation of the molecules.

322. The specific heat of a *gram-molecule* of any gas or vapor—that is, the number of calories (gram degrees) of heat required to raise the temperature of one gram-molecule of any gas or vapor one degree centigrade, under constant pressure—is composed as follows:

A.	*External work*.................	2	calories.	(*G. Schmidt.*)
B.	*Internal work*..................	p	“	(————)
C.	*Actual energy of motion* —			
	a. Vibration of the n atoms...	n	“	(*Naumann.*)
	b. Motion of translation........	3	“	(*Clausius.*)
	c. Motion of rotation............	k.I	“	(*Hinrichs.*)
	Total specific heat of gram-molecule (Hinrichs)*......	$S=5+n+p+k.I$	calories	

Here n is the *number* of atoms in the molecule, k a constant, the same for each series of like compounds, and I the maximal moment of inertia (303, 314). The name in parenthesis is that of the scientist who determined the corresponding term in the specific heat. For gases proper, p is zero, according to *Clausius*.

323. For the alcoholic serials, the specific heat, s′, of which has been determined by *Regnault*, for a volume equal to that of one gram of atmospheric air, we have the observed value of the specific heat of a gram-molecule, $S' = 28.94\ s'$. (See 79.) The calculated values are, according to 322,—

$$S = 5 + n + 3.500 + 0.125\ I;$$

or the internal work is $p = 3.5$ and $k = 0.125 = {}^1/_8$.

These calculated values, S, give the observed values, S′, upon the addition of a small correction: $d = S' - S$.

324. The following *table* contains the numerical results, where M is the total mass (molecular weight, 313):

NAME.	EMPIRICAL FORMULA.	M.	I.	n.	S′.	S.	d.	s′.
Methyl alcohol......	CH_4O	32	8	6	14.64	15.50	—0.86	0.506
Ethyl alcohol........	C_2H_6O	46	26	9	20.87	20.75	+0.12	0.720
Aceton..................	C_3H_6O	58	44	10	23.91	24.00	—0.09	0.826
Ethyl ether...........	$C_4H_{10}O$	74	90	15	35.52	34.55	+0.03	1.227
Sulph-ethyl ether...	$C_4H_{10}S$	90	106	15	36.06	36.75	—0.69	1.246
Acetic ether..........	$C_4H_8O_2$	88	106	14	35.25	35.75	—0.50	1.218

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* Comptes Rendus, June 2, 1873.

It will be observed that the errors, d, are small, and inside the possible errors of the experimental determinations.

325. Before we had shown that the rotation of the molecules in the gaseous state represents a comparatively great amount of energy, all attempts at calculation of the specific heat of vapors were failures, because they left too large a residual value unaccounted for. Thus, in *Naumann's* Thermochemistry,[*] the residual value amounts to 126 per cent of the calculated value for the specific heat of the vapor of turpentine oil — the calculated value being 30.4, while the observed value is 68.8.

326. The specific heat of liquids will contain as term the minimal moment of inertia of the molecule — but at the same time a vastly greater internal work, p. The specific heat of solids contains no term depending on the rotation of the molecule at all — only the internal work of about the same amount as in the liquid state. At the same time, the external work in the expansion of solids and liquids is nearly zero. (See Section III.)

These general results follow readily from our theory of the molecular motions of the three states of aggregation. (See 308.) Further developments on this subject will be found in our special treatise on Molecular Mechanics.

327. Only one extremely interesting application of the preceding principles may yet be made here — namely, *the determination of the chemical constitution of benzol by means of the specific heat of its vapor.*

Regnault has found that $s' = 1.011$; consequently, the specific heat of one gram-molecule of benzol vapor is 29.26 calories.

328. If we extend the formula of 323 to benzol, C_6H_6, we shall have $n = 12$; and, consequently,—

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[*] *A. Naumann*, Grundriss der Thermochemie. Braunschweig, 1869; p. 49.

$$29.26 = 5 + 12 + 3.5 + 0.125\ I,$$

from which follows the maximal moment of inertia, $I = 70.08$.

329. But six atoms CH in one line would give a maximal moment of inertia of 227 — much greater than the above, 70. Hence, the atom of benzol is not linear — agreeing with the fact that benzol is saturated, while the preceding constitution would give it a valence of 8. Any other linear structure will also give a moment of inertia much greater than the above.

If, however, the six atoms CH form a *ring* of radius r, the maximal moment of this ring-atom, C_6H_6, will be $I = 6(CH) . r^2 = 78 . r^2$. Hence, the above value of $I = 70$, determined from *Regnault's* observation of the specific heat of benzol vapors, gives —

$$r^2 = \tfrac{70}{78} = 0.8975;$$

and consequently $r = 0.947$ (the radius of gyration, 313).

330. This constitution of benzol, resulting from the determination of the specific heat of its vapors, agrees most completely with the constitution adopted by modern chemists (*Kekule'*), on account of its highly pronounced chemical characters, and represented in Fig. 12 (compare 216); for the distance between the centers of two carbons united by two atomicities is a little *less* than 1.00, while the distance between two carbon-atoms united by one atomicity has all along taken as unity, or 1.00. Consequently, the mean distance of the six carbons in Fig. 12 is not quite equal to 1.00. Since in any hexagon the radius is equal to the side, the radius of the circle passing through the centers of the six carbon-atoms of benzol is a little less than 1.00 — that is, it agrees completely with the above determination from the specific heat of benzol vapors, according to which this radius is 0.053 *less* than 1.000.

Section XIV. Ebullition.

331. The *boiling point*, t° C, of any liquid is one of its most important physical characteristics — for it *is that degree of temperature at which the vapor-tension of the liquid exactly balances the atmospheric pressure.* (Chem. 71.)

Hence, the boiling point of each compound is determined experimentally with as much care as possible, in the manner indicated in Chem. 64. Its value is always recorded in even the shortest description of the compound. (See Sections VII. to XI.)

332. It has long been known that the boiling points of *similar serials* exhibit certain apparently simple regularities. Thus, in the paraffin series (135) the boiling point rises about 31° for each additional link CH_2 added to the compound. The monatomic acids (184) show an increase in the boiling point of about 22° for each additional link CH_2; the monatomic alcohols show an increase of about 19°, etc.

333. These apparent regularities have led the older school (represented by *H. Kopp*) to think that the boiling point of serial compounds can be calculated in some simple manner from the empirical formula of the compound — at least for certain larger groups of serials.*

334. But these apparent regularities vanish as soon as even in the same series of compounds the terms are extended a little further. The lines determined by the boiling points as ordinates to the number, n, of carbon atoms as abscissæ are not straight, but curved. (Induct. 18.) Besides, the great difference in boiling point of the isomers represented by the same molecular formula constitutes the most absolute condemnation of all such crude empirical rules. Thus, butyl alcohol boils at 116°, ether at 34°—yet both have the formula $C_4H_{10}O$. (Compare 164 to 167.)

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* Thus, for certain acids, the addition of C is said to increase the boiling point 14.5°, while the removal of H raises the boiling point 5°. This would be very simple and nice, but, fortunately, it is not true. (See *Kopp*, Theoret. Chemie, II. Aufl., 1868, pp. 202—207, for full particulars in regard to this style of empiricism, which culminates in recent articles of *Groshans* in Berichte Deutsch. Chem. Ges.; Berlin, 1878.)

335. Not without much labor has the author freed himself from the still dominant influence of this school of empirics (333); and, since mental arithmetic is somewhat easier mastered than the laws of mechanics, we shall not be surprised if this school remains dominant for some time to come. Nevertheless, we will venture to give a few of the general laws which we have discovered in regard to the boiling point of serials. A more complete exposition of this subject will be given in our special treatise on *Molecular Mechanics.*

336. The *paraffins* constitute the organic elements proper (175, 135). The boiling point, t_n, of the paraffin containing n atoms of carbon we find to be—

$$t_n = 420.\ \log n - 256°;$$

or, in absolute temperatures (42, d)—

$$T_n = 420.\ \log n + 17°.$$

337. No straight line can represent the boiling points of these paraffins, so carefully determined by *Schorlemmer*[*] for n = 4 to n = 8. (See 338.) The great fact of a gradual decrease in the difference of boiling point cannot be represented except by the logarithmic function.

338. Fig. 37, Plate II., represents the *boiling-point curves* determined by the following table of observed values of the boiling points in centigrade degrees:

n =	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Paraffins	.....	.....	.....	1	38	70	99	124	.....	.....
Ethers	.....	−21	11	34	.....	92	112	132	.....	176
Monamines	.....	19	50	69	94	126	146	170	.....	.....
Ketones	.....	.....	56	81	101	128	144	.....	.....	.....
Alcohols	67	78	96	110	130	150	164	182	200	212
Acids	100	117	141	161	175	198	212	236	260	.....
Chlorides	−22	11	.....	.....	102	130	.....	180	.....	.....
Bromides	13	41	71	92	121	.....	.....	.....	.....	.....
Iodides	46	72	102	129	147	165	....	221	.....	.....
Iso-iodides	.....	.....	89	121	.....	.....	.....	.....	.....	.....

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[*] Jahresbericht, 1871, p. 369. For n = 12 and 16, he had evidently isomerics.

It is apparent that the "rule of three" is not immediately applicable to this question of theoretical chemistry (333); for the resulting lines are *curves*, and not straight lines. (Induct. 13.)

339. The isomers of the monovalent alcohol series containing *six* carbon atoms may be taken as a good example of isomers. (See 334.) They are enumerated in the following table, wherein, for the sake of convenience, each isomer is designated by a letter:

	NAME.	BOILING POINT,
A.	HYDROCARBONS, $C_6H_{14} = 86$.	t° C.
	a. Hexane	69–70
	b. Dimethylpropylmethane	62
	c. Tetramethylethane	58
B.	HYDROCARBON OXIDES, $C_6H_{14}O = 102$.	
	Ethers:	
	d. Isopropylether	60
	e. Methylisobutylether	80
	f. Methylamylether	92
	Carbinols:	
	g. Hexylalcohol (Pentylcarbinol)	151
	h. Methylbutylcarbinol	136
	(*i.* Methylbutylketon	127)
	k. Methyldiethylcarbinol	120
	l. Dimethylisopropylcarbinol	115
C.	AMINES, $C_6H_{14}NH_2 = 102$.	
	m. Triethylamine	87
	n. Hexylamine	121

It will be noticed that the isomeric oxides range in their boiling point from 60° to 151°, or full 91°, although their molecular formula is exactly the same; thus totally disproving the idea that the boiling point is a simple arithmetic sum of any "boiling point equivalents." (Compare 334.)

340. Consequently, the boiling point of compounds is not a function of the atomic weight simply, but of the atomic weight and molecular structure jointly (160). I have found that the *maximal moment of inertia* of the atom is the mathematical expression of these independent variables (weight and form, or structure*); for, when a liquid boils, its vapor permanently balances the atmospheric pressure (331) — that is, at a given pressure the liquid boils at that temperature for which its temperature suffices to keep the molecules in the gaseous condition, rotating around the maximal axis (308).

341. Other things being equal, it follows, from this, that *the boiling point of any liquid depends on the maximal moment of inertia of its molecules, increasing and decreasing with the same.*

This may be represented by —

$$T = F(I),$$

where F represents the function, I the maximal moment of inertia, and T the absolute boiling point — $T = 273 + t^\circ$ C. (Compare Induct. 9.)

342. For isomers, M, the total mass of the molecule, is the same (312); hence, the moment of inertia of isomers is proportional to R^2, the square of the radius of gyration (313). If, for the sake of convenience, we represent R^2 by i — that is, if we put (see 314) —

$$R^2 = \frac{I}{M} = i,$$

then the above (341) may be expressed as follows:

The boiling point of isomers depends on the maximal radius of gyration, $R^2 = i$, *of the molecules, increasing and decreasing with the same.*

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* That the boiling point depends on the *form* of the atoms, I asserted as early as 1857, in various publications. That it is dynamically dependent on the moment of inertia, I first published in 1872.

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343. The boiling point of the isomeric hydrocarbons, C_6H_{14}, is, in accordance with 342—

$$t' = 52.25° + 5°. i,$$

as may be seen from the following table (compare 339):

	M.	I.	i.	t'.	t.
a................	86	257	3.06	69.0	69-70
b................	86	147	1.75	62.0	62
c................	86	81.5	0.95	58.0	58

344. The boiling point of the *isomeric ethers*, $C_6H_{14}O$, may be calculated by—

$$t' = 37° + 25\ i + 2.2\ i^2,$$

as appears from the following differences, d, between the observed, t, and calculated, t', boiling points (see 339):

	M.	I.	i.	t'.	t.	d.
d..........	102	85	0.83	59.8	60	0.7
e..........	102	155	1.52	80.1	80	0.1
f..........	102	195	1.91	92.7	92	0.7
(*h*..........	102	320	3.15	137.5	136	1.5)
(*g*..........	102	355	3.48	150.6	151	0.4)

The carbinol g is necessarily common to ethers and carbinols proper; the agreement with h is not essential.[†]

345. The boiling point of the *isomeric carbinols*, $C_6H_{14}O$, may be calculated by—

$$t = 110.6° + \tfrac{10}{3}\ i^2,$$

as will be seen from the following comparison with the observed values, t, of 339:

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[*] See our paper on these compounds in Report of American Association for the Advancement of Science, Chicago, 1868.

[†] See Schorlemmer, Berichte Deutsch. Chem. Ges., Berlin, 1870, p. 616. Either observation h in 339 is erroneous, or belongs to another isomer.

	M.	I.	i.	t'.	t.	d.
g.......	102	355	3.48	151.0	151	0.0
h.......	102	320	3.15	143.7	141*	2.7
(*i*........	100	222	2.22	127.0	127	0.0)
k.......	102	179	1.75	120.8	120	0.8
l.......	102	116	1.14	114.9	115	0.1

346. Our theorectical law in regard to the boiling point of isomers (342) is, therefore, most remarkably *confirmed* by the numerous isomers of monovalent alcohol serials containing six carbon atoms. It is equally well confirmed by all other isomers thus far investigated by us. The curves (Fig. 38, Plate II.) represent these facts graphically — the observed boiling points being marked by dots, the letter referring to the compounds as enumerated above and in 339.

347. We may therefore consider the introduction of the maximal moment of inertia into molecular science as one of its most important independent variables accomplished. The thermometer has indeed become the instrument whereby the dimensions of the molecules are determined. (See 224, 330.)

348. The relation of the boiling points of the different *series* of monovalent alcohol compounds is indicated by the following simple application of the law of 341:

Let the maximal moment of inertia of the paraffin of n carbon atoms be represented by I_n. Its mass, a_n, is then increased by the addition of a mass, m, at a distance, d, from the center of gravity of the paraffins in order to produce the ethers, alcohols, etc. (See formulæ in 179 to 200.)

Thereby the maximal moment of increases, according to elementary mechanics:

$$D_n = \frac{a_n m}{a_n + m} \cdot d^2.$$

349. Now, in ethers d is smallest, the oxygen m being added somewhere along the linear paraffin atom, and least of all in simple ethers, O being added exactly in the middle. Hence, the boiling point of the simple ethers is lowest, and for mixed ethers increases with d — *i, e.*, with the difference between the two constituent radicals (188). The primary alcohol forms the last term in this series — for here d is greatest, being equal to half the length of the paraffin atom. Finally, the secondary and tertiary alcohols have different, smaller values of I_n, and thus form a new series. (Compare 343 to 346.) Finally, in acids $m = 2O - 2H$ is added to the extremity; hence the boiling point of acids is still higher than that of the alcohols. Compare the curves of Figs. 37 and 38, Plate II., for a confirmation of these results.

350. The distance between the curves — or the differences between these boiling points — diminishes with increasing values of n; for the moment I_n increases as the cube, while D_n increases as the square of the atomic dimensions. The curves of Fig. 37, Plate II., also prove this result of our theory on simple inspection.

351. Numerically, this is expressed by saying that the *increase*, b, of the boiling point of the alcohol and acid over that of the corresponding paraffin is proportional to the value of the fraction $f = \frac{am}{a+m}$ for each (348). In other words, the ratio, $^b/_f$, should be the same, nearly, for alcohol and acid, for each value of n separately.

The following shows that such is the case:

		f.	b.	$^b/_f$.	MEAN.
$n = 4$:	Alcohol	12.5	110°	8.8	8.2
	Acid...........	20.6	160°	7.7	
$n = 8$:	Alcohol	14.0	62°	4.4	4.5
	Acid...........	25.0	116°	4.6	

352. These few deductions from our theory will be sufficient in these general principles of chemistry. The existing observations confirm the theory in every particular. *The rotation of the molecules of gases around their maximal axis*, being independently established by the specific heat of vapors (324) and the boiling point of liquids (339 to 351), in harmony with the chemically established constitution of serials, may now be considered as a reality. Indeed, the molecules *have* a motion of rotation similar to that exhibited by the cosmical molecules — the planets.

353. In conclusion, we call attention to the simple explanation of boiler explosions contained in this theory. Water — or any other liquid — may evidently be overheated at any given temperature, provided the particles be not disturbed; the rotation will then continue about the minimal axis. But a slight disturbance will quickly change the whole mass to vapor — the particles revolving around the maximal axis.

The cooling of water below its freezing point, and its sudden solidification upon a disturbance, is also readily understood by the molecular rotations.

The so-called *continuity* of the liquid and gaseous conditions, discovered by *Andrews*, may also now be explained.

354. The laws governing the boiling points of substitution products proper (Cl, Br, Io, etc.), as well as the application of these principles to aromatic compounds, must be sought in our *Molecular Mechanics*. The theory here indicated explains the most intricate phenomena in general, and frequently permits the accurate calculation of the variations in boiling point produced by a given chemical process. Hence, it can also predict the results to follow when compounds are heated in closed tubes — such as Hofmann's Atom-Wanderungen in the Molecules.

355. The vapor pressure, P, in atmospheres (of 760 mm mercury each) which corresponds to any given temperature, t° C, for any given liquid, has, thus far, not yet been expressed by a general formula. In other words, the relation between vapor-tension and temperature is not yet known, except experimentally. (Compare Chem. 72.)

The theoretical importance of this subject is so great, that it may excuse the submission of a simple first approximation which we discovered a few years ago.*

356. Our formula is—

$$P = \left(\frac{\tau}{k}\right)^6$$

where P is the pressure of the vapor in atmospheres; $\tau = a + t$, the distance from the *zero point*, at which the liquid begins to give off vapors, to the temperature, t° C, for which the pressure is P; and k, the distance from the zero point to the boiling point of the liquid, for which $P = 1$. k and a are constants.

For $a + t = o$, the value of t is $-a$, which we call the *zero point* of the liquid. It evidently is that *temperature at which the liquid ceases to form vapors.*

For $a + t = k$, the pressure is one atmosphere—that is, $t' = k - a$ is the *boiling point* of the liquid.

357. The following table gives the values of these constants for five gases and three liquids. By substituting these values in 356, the pressure of the vapor for any given temperature may readily be calculated.† The interval of temperature for which the formula gives approximative results, is given in the last double column.

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* The intricate transcendental formula of *Biot*, adopted by *Regnault*, is also only approximative and empirical. The values of α and β therein are so near unity as to indicate that the real function is not transcendental.

† Best by logarithms—four places will suffice.

$$\log P = 6\,[\log (a + t) - \log k].$$

If the pressure, p, is required to be in millimeters, add log 760 — 2.8808 to log P.

NAME.	FORMULA.	k.	a.	t′.	INTERVAL.
Carbon dioxide............	CO_2	116.8	218.7	—97.4	—45 to 0
Hydrogen chloride........	HCl	118	205	—87	—73 " 4
Hydrogen sulphide.......	H_2S	142	210	—68	—73 " 4
Arseniuretted hydrogen	H_3As	136	196	—60	—73 " 4
Ammonia	H_3N	138.9	180.4	—41.5	—36 " 6
Carbon bisulphide........	CS_2	195	149	46	—20 to 120
Wood spirits......	CH_4O	158.5	91.71	66.75	—20 " 120
Alcohol (absolute)........	C_2H_6O	153	74.6	78.4	—20 " 120

358. For the following two gases and four liquids, the formula of 356 gives results which are not sufficiently close, except a small term, increasing with t, be added to the constants a and k, as shown in the following table:

NAME.	FORMULA.	k.	a.	t′.	INTERVAL.
Nitrous oxide...	N_2O	$105 + {}^1/_7 t$	$188 + {}^1/_7 t$	—83	—80 to 0
Sulphur dioxide	SO_2	$86 + 0.6 t$	$104.2 + 0.6 t$	—10.7	—10 " 20
Ether (common)	$C_4H_{10}O$	$160.5 + {}^1/_6 t$	$125.5 + {}^1/_6 t$	35	—20 to 120
Chloroform	$CHCl_3$	$177 + 0.1 t$	$117 + 0.1 t$	60	20 " 110
Benzol.............	C_6H_6	$149 + 0.27 t$	$69 + 0.27 t$	80	
Water...............	H_2O	$159.7 + 0.071 t$	$59.7 + 0.071 t$	100	0 " 12

359. The student calculates *tables* from these equations, giving the values of the pressure for every twentieth degree. Thereafter, the values so obtained should be represented on a double-page co-ordinate sheet at the close of this volume. By using the scales, vertical, $P = 1$ atmosphere to 5 cm (or 1 mm to $^1/_{50}$ atmosphere) and t horizontal, one degree to the millimeter, the most important results will be represented between the limits $P = 0$ to $P = 3.7$ and $t = -100°$ to $t = 150°$.

Upon this same sheet should then be entered, for each line, a number of actual observations, to compare the result of observation with our formula. A closer test is, of course, obtained by calculating the value P for the given t for which an observation has been made; but the above graphical test is, for the student, more instructive and much easier.

360. As stated, we give the equation (336) simply as a sufficiently close, and very convenient, *general* approximation, and not for the true law. But while in chemical practice our formula is quite sufficient, and its constants easily determined from observation (see Induct. 28), we believe it to be nearer the true rational formula than the formula of *Biot* (357).

Section XV. Dissociation.

361. *Dissociation is the decomposition of a compound by heat alone.* (Chem. 93.) It is now accepted that all compounds will dissociate, if only their temperature be raised sufficiently high. (*Deville.*)

A great many examples of dissociation have been given in the *Elements of Chemistry.* See also some cases of gradual dissociation above (32).

362. Thus, lead nitrate, $Pb(O_3N)_2$, when exposed in a hard glass tube to red heat, will dissociate. In the tube will remain lead oxide, PbO, while nitric peroxide, N_2O_4, will condense to a yellowish liquid in a cooled receiver; at the same time, oxygen passes off as gas. This dissociation is represented in Fig. 24 — a figure which is only given as an example how graphically to represent a simple dissociation.

The nitric peroxide dissociates readily when moderately heated, as we shall see further on (372); it yields the red vapors of nitrogen dioxide, NO_2, or *nitryl.* The peroxide may therefore be called *dinitryl.*

362. But even the most stable compounds, such as HCl, H_2O, etc., can be dissociated. *Deville* used for this purpose his *hot-cold tube.* It consists of a narrow copper tube, surrounded by a wider porcelain tube. In the space between the two tubes the gas can be made to circulate, Cold water flows through the inner copper tube, while the outer porcelain tube is exposed to the heat of a furnace. The gas meets the very hot porcelain, whereby the compound is decomposed. The resulting mixture finds the cold metal tube in close proximity, so that it cannot re-combine.

The electric spark has nearly the same action—it is also hot-cold.

363. By this hot-cold tube, *Deville* has, from steam (near 2000°), obtained a mixture of oxygen and hydrogen. Hydrogen chloride dissociated about 1500°; carbon dioxide, about 1300°; sulphur dioxide, about 1200°. Ammonia and other gases were also thus dissociated.

It is now well understood that even in the flame of the oxyhydrogen blow-pipe (Chem. 104) the combustion is not complete, because the temperature produced (about 2000° C) is above the temperature of the partial dissociation of water. By burning these gases under *pressure*, thereby retarding the dissociation (see 381), a much higher temperature may be produced.

364. One of the most instructive cases of dissociation is that of *ammonium carbamate*, $NH_4O\text{-}CO\text{-}NH_2$, at or above 60°, giving $2NH_3$ and CO_2. When these same (dry) gases meet at common temperature, they again unite to the white, solid carbamate, which at —60° gives off no vapor at all. Fig. 25 represents this circulation of the two gases, produced by a simple change in temperature. (See 194.)

The formation of sal-ammoniac at common temperatures, and its dissociation at higher temperatures, has already been noticed. (See 64.)

365. The dissociation of a compound does *begin* at a certain temperathre, t′, and is *completed* at a certain higher temperature, t″. Below the first temperature, the compound can exist, but not above the second. The dissociation is most rapid at a temperature about equally distant from the lower and higher limits. This temperature, τ, is often called *the temperature of dissociation.* At the same time, the *pressure* on the gas also very much affects the process of dissociation.

We shall now give a synopsis of the general results obtained in regard to the process of dissociation as function of temperature and pressure.

366. *The velocity of dissociation can be represented by the probability curve* (Curve v, Fig. 39, Plate II.), also called the *binomial* (*Horstman*, 1868).

Let the temperature be divided into equal intervals in such a manner that τ is in the middle of one. Let these intervals be counted from this as o — downwards *negative*, upwards *positive*,— as first, second, etc., in general n^{th} interval. Then the *velocity* of dissociation, v, in the n^{th} interval will be represented by the *equation** *of the probability curve* —

$$\log v = a - b . n^2,$$

where a is the velocity during the interval of $n = o$ at the temperature of dissociation, and b a constant.

367. The total percentage, S, dissociated up to any given temperature is, of course, represented by the *area of this curve of probabilities up to that temperature* (Curve S, Fig. 39, Plate II.) The area of the curve above that temperature represents the amount yet undissociated.

368. These laws may be established theoretically. The temperature of the body under dissociation, as indicated by the thermometer, is simply the *mean* temperature of the molecules of the body. The temperature —*i. e.*, velocity of motion (see 42, e,)— of the individual molecules is above and below this, distributed according to the law of probability.* Hence, the velocity of dissociation will be governed by the same law.

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* This form is most convenient for practice. We have given it in our School Laboratory, Vol. II., 1872. p. 32, *where it is experimentally established by the drawing of balls from an urn.*

369. While this is not the place to fully give the theoretical demonstration just referred to (368), we must show that the law of probability governs the process of dissociation *de facto*. We must prove that the laws of 366 and 367 are demonstrated by *experiment*.

370. The molecular weight, w, of the gas under dissociation is determined experimentally (53) for as many different temperatures as possible. (Curve w, Fig. 39, Plate II.) If now the molecular weight of the gas undissociated be m, and if by dissociation its molecules resolve themselves, as most common, into two† molecules, then we can, from the actually observed weight, w, readily calculate the percentage dissociated.

371. At any given temperature for which the molecular weight, w, has been experimentally determined, S molecules out of every hundred have dissociated, while $S' = 100 - S$ are yet undissociated. (See 367.) Consequently, the original 100 molecule-volumes, which weigh 100.m, now occupy the volume $2S + S$. Since each of these, by experiment, has the weight w, the total weight of the $2S + S'$ volumes is $(2S + S')$ w. As the total weight cannot change by dissociation, we have —

$$(2S + S')\,w = 100.m.$$

Consequently —

$$S = 100\left(\frac{m}{w} - 1\right) \text{ per cent dissociated;}$$

$$S' = 100\left(2 - \frac{m}{w}\right) \text{ per cent undecomposed.}$$

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* Exactly as the height of the men of a given age, in a given nation, has a certain mean value from which the individuals differ, the number and magnitude of these differences being governed by the same law of probability (*Quetelet*). This law really governs all peculiarities of *individuals in a mass*—the molecules in a body as well as the men in a nation.

† If any other number, the method here given will also be applicable—only the formulæ will become a little less simple.

372. From the many series of determinations of the molecular weight as function of temperature, t, we select those of *H. Deville* and *Troost* on dinitryl, or nitric peroxide, N_2O_4, which *colorless gas* readily dissociates into nitryl, NO_2 (nitrogen dioxide), a gas of deep red color.

Now $N_2O_4 = 92$, and $NO_2 = 46$. Each molecule of dinitryl dissociates into two molecules of nitryl, so that the percentage, S, dissociated can be calculated by **371**, if the values of w observed are substituted in the formula given.

t.	w.	S.	t.	w.	S.
26.7°	76.6	20.0	90.0°	49.8	84.8
35.4°	73.2	25.7	100.1°	48.5	89.2
39.8°	71.2	29.2	111.3°	47.7	92.7
49.6°	65.7	40.0	121.5°	46.8	96.2
60.2°	60.2	52.8	135.0°	46.2	98.2
70.0°	55.6	65.6	154.0°	45.7	100.0
80.6°	52.1	70.6	183.2°	45.4	100.0

373. By taking the temperature, t, as abscissa, and the observed molecular weight, w, as ordinate, the *curve* of the molecular weights (Curve w, Fig. 39, Plate II.) will result. Its beginning is evidently about —30°, where $w = 92$, the molecular weight of the *colorless dinitryl*, $N_2O_4 (S = 0)$; it ends about 150°, where $w = 46$ $S = 100$), or all dinitryl is dissociated into the *deep red colored gas nitryl*, NO_2. At about 58° the original gas is half decomposed; hence $\tau = 58° C$ is the temperature of dissociation of dinitryl. The dissociation requires, from beginning to end, a range of about 180° in temperature. Compare 60, which will now be more fully appreciated.

374. Also construct the curve S (Fig. 39, Plate II.) as ordinate for t as abscissa, on the co-ordinate sheets at the close.* To the *left* of this curve, we have the undecomposed dinitryl; to the right, the per cent dissociated. This curve has the characteristic form of the curve of 367, expressing the *sum* of the probabilities. That it really *is* this peculiar curve, we can readily demonstrate in the following manner. (School Laboratory, 1872, p. 34; and Induct. 21.)

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* Convenient scale: each per cent, 1 mm, and each degree C, 1 mm.

375. From the curve of S, carefully drawn, determine the velocity, v. of dissociation for each tenth degree—that is, the number of per cent dissociated from 5° below to 5° above the temperature for which the velocity is to be determined.* Construct the curve determined by these values of v for every tenth degree below and above 58°. Then it will be found† that the constants in 366 for this case are—

$$\log v = 1.12 - \tfrac{3}{100} n^2.$$

(See Curve v, Fig. 39, Plate II., constructed from these calculated values.

376. The following table gives the temperature, t; the corresponding value of n; the observed velocity, v; the velocity of dissociatian, v′, calculated by 375; and the correction, c, to be applied to the latter to produce the observed value:

LOWER HALF.					UPPER HALF.				
t.	n.	v.	v′.	c.	t.	n.	v.	v′.	c.
58	0	15.0	13.2	1.8	58	0	15.0	13.2	1.8
48	—1	10.0	12.5	—2.5	68	1	12.5	12.3	0.0
38	—2	8.5	10.0	—1.5	78	2	8.5	10.0	—1.5
28	—3	6.5	7.1	—0.6	88	3	7.5	7.1	0.4
18	—4	……	4.4	….	98	4	3.5	4.4	—0.9
8	—5	……	2.3	….	108	5	3.0	2.3	0.7
—2	—6	……	1.1	….	118	6	2.1	1.1	1.4
—12	—7	……	0.5	….	128	7	2.0	0.5	1.5
—22	—8	……	0.1	….	138	8	1.0	0.1	0.7

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* Thus, the velocity of 58° is 15, because at 53° 42.5 per cent are dissociated, and at 63°, 57.5 per cent.

† By drawing the *straight line* determined by n^2 as abscissa, and the logarithm of the corresponding *observed* velocities, v, as ordinates. (Induct. 21.) Only two places need be retained in the logarithm.

377. Construct these values of v′ (to the scale of 2 = 1 cm) for n (one to 1 cm) on one of the co-ordinate sheets. The curve (Plate II., Fig. 39, Curve v, smaller scale,) thus resulting, is the *probability curve*, represented by the equation in 375. Also enter the observed values of v as points for the same n; they will all be found quite near the curve (see figure). The deviations, c, are very small, when we remember that the observed values, v, are obtained by a complicated process.

Accordingly, we may consider it experimentally demonstrated that *the law of probability regulates the rate of dissociation* of nitric peroxide. (See 366.) By reducing other observations, the student will find that this law applies in all cases.

378. The influence of *pressure* on dissociation is very marked. In general, for any given temperature, *the dissociation has a limit dependent on the pressure of the gaseous product of dissociation.*

379. It has been found that this pressure is related to the temperature in precisely the same manner as the pressure of a vapor to the temperature of the boiling liquid. (See 355.) Hence, our formula (356) is also applicable to the *pressure of dissociation;* that is, the pressure, P (in atmospheres), of the gas produced by dissociation is proportional to the sixth power of the temperature, τ, of the dissociating body, this temperature being counted from the temperature, —a, at which dissociation begins. Also, k is the number of degrees from this point, —a, to the temperature at which the tension of dissociation equals one atmosphere. (Compare 356.)

380. The following *table* gives some of the results of observation expressed by our formula (356). (Compare 357.)

NAME.	FORMULA.	k.	a.	t′.	GAS.
Ammoniated CaCl^{ide}.........	$CaCl_2 + 8H_3N$	118	88.8	29.2	H_3N
Ammonium Carbamate...	$(NH_3)_2CO_2$	120	60	60	H_3N CO_2
Ammoniated CdS^{ate}.........	$CdO_4S + 6H_3N$	250	176.4	73.6	H_3N
Hydrated H-Na_2P^{ate}.....	${}^{Na_2}_{H}O_4P + 12H_2O$	155	59	96	H_2O
(Water........	H_2O	160	60	100	H_2O)
Sal-Ammoniac............	NH_4Cl	251	—89	340	NH_3 HCl
Calcite.........	CaO_3C	740	—346	1086	CO_2

Water has here been inserted from 358, merely to compare its free vapor tension with that resulting from water of crystallization.

381. The signification of these figures will not need further explanation. However much of the dissociable substance may be present, it will dissociate at any given temperature only until the pressure of the gas produced equals the pressure determined by the law of 379, using the constants of 380.

Thus, for $t = 860°$, the above constants give, by my formula (356) for calcite, a pressure of dissociation of 0.1124 atmospheres, or 85.4 millimeters mercury. *Debray* found the tension of carbon dioxide on calcite, at this temperature, 85 mm. Now, if the temperature remains the same, this pressure will also continue the same. If some gas is removed, enough will separate again from the calcite yet undissociated to restore the above pressure.

382. Hence, it is possible to construct a *dissociation thermometer;* the pressure of the resulting gas constitutes the measure of the temperature. The vessel containing the substance may be at a considerable distance from the manometer which measures the pressure and communicates with the vessel by means of a narrow metallic tube.

Not enough experiments have been made to secure a substance which is not changed in its molecular condition by long protracted use for such a purpose. In time, the re-absorption upon sinking temperature seems to become gradually more slow.

383. The phenomenon of dissociation is readily explained, if we consider the constitution of molecules (41) and the motions of the atoms in the same (322; also, 42, e). The vibrations of any atom, m, in the molecule represents an actual energy, or *vis viva*, $m . v^2$, measured by the absolute temperature, T; while the atom itself is retained in its position of equilibrium in the molecules by a certain force, f, of attraction.

384. As now T may be indefinitely increased, while f has a definite value, it follows that the atom, m, must fly off from the molecule, as soon as the velocity, v, of the vibration of the molecule, by the increase of the temperature, T, has increased the *vis viva* of vibration beyond the above limit of the force of attraction, f. The result is, the dissociation of the molecule.*

The rate of dissociation as expressed by the law of probability, and also the relation to pressure, follow from this explanation. (Compare 368 to 379.)

385. The precise manner in which a molecule will dissociate under given circumstances, may also be predicted from the rational formula of the same.

Show, from its graphical formula, that alcohol dissociates into hydrogen, water, and acetylene, when passed through a red hot tube. Notice the rotation of about 90° of the carbon atoms towards one another.

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* This explanation may be illustrated by two lead weights, connected by an elastic string. Holding one of the weights in a hand, the oscillation up and down of the latter will make the other weight oscillate towards the first. By increasing the excursions, the lower weight finally snap the elastic string, and thus dissociate the molecule.

386. The gradual dissociation of blue vitriol, $CuO_4S + 5H_2O$, may now also be understood. (Chem. 91 to 95.) The water of crystallization passes off first—it being the most volatile, and also situated on the outskirts of the molecule. Four of the atoms of water pass off easier than the fifth; hence, this last one is held by a greater force of attraction (383). At a red heat, SO_3 flies off, which again readily dissociates into O and SO_2. Finally, the CuO remaining has, thus far, never been dissociated—the temperature has not been raised high enough for that (361).

By passing the two gases, SO_2 and H_2O, through the hot-cold tube of *Deville* (362), they dissociate into their elements—proving that these elements in the binary are held more firmly together than the atoms in the original molecule of blue vitriol. Fig. 26 represents this gradual dissociation of blue vitriol. The points of application of heat are marked by cross-lines.

387. Fig. 26 is to serve simply as a model how to graphically represent dissociations. Represent, in this manner, a number of the cases treated of in this volume, and in the Elements of Chemistry. One of the simplest cases is the dissociation of platinic chloride, which at 200° loses one molecule of chlorine, and at a beginning red heat loses the other molecules of chlorine—thus being completely dissociated into its elements. (See 110).

388. In the preceding cases of dissociation, the interval of temperature from the beginning to the completion of the process was of considerable extent. (See 365.) Thus, for dinitryl this interval extends from —42° to 158°, or over 200°. The more extended this interval, the more gradual the dissociation; the less extended, the more sudden the dissociation.

389. *When a dissociation is very sudden, and yields* *gaseous products, it is termed a detonation.* Thus, the vapor of methyl nitrate dissociates suddenly when heated to 150° — it is said to detonate. (Compare foot-note to 126.)

The reason of this sudden dissociation may be read from the structural formula of the compound. As soon as the thermal vibrations of the atoms in the molecule CH_3-O_3N have reached a certain degree, the carbon and hydrogen will unite directly with the oxygen to CO_2 and H_2O, leaving N and H free. Two molecules of methyl nitrate thus give two molecules of carbon dioxide, two of water, one of hydrogen, and one of nitrogen. These being all gases, a sudden expansion is caused by the dissociation.

390. In general, we may say that *detonating, or explosive, compounds contain the atoms united in the molecule in an unstable equilibrium.* Thus, in nitro-glycerine (207, Fig. 10, g,) the 2O is, by nitrogen, held far from the carbon for which it has the greatest attraction. So long as the molecule is not violently shaken — either mechanically, from without, or thermally, by an increase of temperature — the atomic oscillations will continue without disturbing the structure of the molecule. But if, by any cause, the atoms be brought sufficiently out of this position, they pass further and further from their forced position in the original molecule, in accordance with their attractions.* Here nitro-glycerine gives $3\,CO_2$, the 3N sliding away from between the C and O_2; also, H_2O from each end of the molecule, and HO is left in the middle; so that from four molecules we shall have: $12CO_2$, $6N_2$, $8H_2O$, and 4(HO) as O_2 and $2H_2O$. Show this in detail. In ordinary applications, nitro-glycerine is exploded by a sudden concussion, produced by a peculiar *fuse.* Evidence of this we have also in the heat produced at the same time, as will be shown in the next section, on Caloration.

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* Precisely as an elastic cone, supported on its vertex, may oscillate in the vertical without falling; but when these vibrations become very great, or if the cone be shaken in any other direction, it will suddenly fall.

Mercury fulminate, $CN\text{-}CHg(NO_2)$, used in percussion caps, also detonates by a blow. It divides into Hg and $2CO\text{-}N$, the latter giving immediately $2CO$ and N_2. (See 128.)

Section XVI. Caloration.

391. The amount of heat produced or absorbed in any chemical process, we shall call the *caloration* of that process.* (Compare Chem. 98, 162, 163.)

392. Unless otherwise distinctly stated, the caloration will be expressed in *gram-degrees* (*calories*, see Chem. 43,) for *one milligram-atom* of the *product* formed in the process. These units are abbreviated gr.° and mgr.at. Thus, one mgr.at. water, formed from its elements (2 mgr. hydrogen and 16 mgr. oxygen), produces 68.4 gr.°. The caloration of the synthesis of water from its elements is, therefore, 68.4.

393. But the mechanical equivalent of heat is 425 (Chem. 80). Consequently, each gram-degree corresponds to 425 gram-meters, or 0.425 kilogram-meters (abbreviation, kgr.m.) Any caloration of x gr.° may, therefore, most readily be converted into mechanical work or *energy* (kgr.m.) by the multiplication of the tenth of x by $4^1/_4$. For example: the synthesis of *one* mgr.at. water, producing a caloration of 68.4 gr.°, represents a mechanical work of $4^1/_4 \times 6.84 = 29.1$ kgr.m.

394. We have selected these units after mature deliberation, because they give the simplest expression of the dynamic changes which characterize chemical processes. It will be understood, that if the process is attended by an absorption of heat, the caloration is negative, as well as the energy of the process. Thus, the formation of one mgr.at. of the most dangerously explosive nitrogen chloride, NCl_3, represents* a *caloration* of —38 gr.°, and an *energy* of —16.2 kgr.m. In other words, the synthesis of 14 mgr. nitrogen and 106.5 mgr. chlorine represents an *absorption* of 38 calories, or an *expenditure* of mechanical work of 16.2 kilogram-meters.

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* *Thomsen* uses the word *Wærmetœnung*, but it is neither well chosen, nor can it be conveniently translated.

395. It is highly instructive to represent these results graphically. The number of kgr.m. energy given is evidently the number of *millimeters* through which a ton (1,000 kgr.) can be lifted by the caloration produced in the process. Hence, the results are immediately constructed, by using the number of energies (kgr.m.) as *millimeters* vertical height in the chart. For example: the synthesis of a milligram-atom of water (18 mgr. water) produces a force which will lift a ton 29.1 millimeters high (393). Also, the explosion of a milligram-atom of nitrogen chloride (120.5 mgr.) produces a mechanical effect sufficient to lift a ton 16.2 millimeters high (394).

396. It will now be understood what is meant by difference in *chemical level.* Hydrogen and oxygen gas in uniting represent, per milligram-atom, the fall of a ton through 29.1 millimeters. To again separate a milligram-atom of water into its constituent gases, requires an expenditure of energy equal to the lifting of a ton through 29.1 millimeters vertical height.

Hence, every cubic centimeter of hydrogen gas produced by a galvanic current represents somewhat more than a kilogram-meter of mechanical work. This expression is given in order to convey a more distinct idea of the power of the galvanic current. (See 51, and Chem. 102.)

397. It is important to distinguish between *actual* and *potential energy.* (Induct. 59.) A kilogram descending one meter, acquires a certain velocity, in virtue of which the kilogram striking any object may exert a mechanical work on the same equal to a kilogram-meter—the precise amount of work required to be done in order to again restore the kilogram to its former level. (Compare Phys. 97 to 100.)

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* *Deville* and *Hautefeuille*, 1869. This number is far from exact (*Thomsen*); but it is certainly negative, and hence may here be used.

Accordingly, a kilogram at any given level is *not* the same, so far as force is concerned, as a kilogram at a level one meter above the former; for it requires the expenditure of one kilogram-meter of energy to lift the lower kilogram to the level of the higher, and the higher kilogram will produce one kilogram-meter of energy in descending to the level of the lower weight.

398. The *potential energy* is, therefore, that energy or mechanical work which is expended in *producing* a position, while overcoming some force. It is not lost, for it re-appears as an equal amount of *actual energy* when the position is lost. Thus, the potential energy of a mixture of two mgr.at. hydrogen and one mgr.at. oxygen is 29.1 kilogram-meters. for so much energy will be produced when the mixture explodes, forming water.

The terms energy of station, or energy of position, would, perhaps, be easier understood; but we have to use the above term, because it has general currency.*

399. We can now numerically complete the chemical equations of chemical processes. (Chem. 162 to 165.) Thus we have, using the values repeatedly quoted in the last few articles, for mgr.at.:

$$2H + O = H_2O + 68.4 \text{ gr.}^\circ;$$
$$\text{or, } 2H + O = H_2O + 29.1 \text{ kgr.m.}$$

$$N + 3Cl = NCl - 38 \text{ gr.}^\circ;$$
$$\text{or, } N + 3Cl = NCl_3 - 16.2 \text{ kgr.m.}$$

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* The same terms are applicable to the mental and social world. Learning a trade gives potential energy to that work. Every new discovery represents an immense amount of brain-work, which helps the diffusion of knowledge and further discovery, and adds to the potential energy of humanity.

400. Of course, *if no occult forces*—that is, forces other than mechanical (Phys. 97, 450)—are admitted, then *these complete equations of chemical processes must remain correct after any algebraical transformation proper.* Thus, if—

$$\begin{array}{l|l} A+X=AX+a & A+Y=AY+y \\ B+Y=BY+b & B+X=BX+x \end{array}$$

then—

$$\begin{aligned} A+B+X+Y &= AX+BY+c \\ &= AY+BX+z \end{aligned}$$

where we must have the calorations—

$$c=a+b \qquad z=x+y$$

In words: *the same system of bodies in the same physical and chemical condition are the* SAME *in* WEIGHT *and* ENERGY. Applications of this principle abound in the following articles of this section.*

401. The accurate *experimental determination* of the caloration of chemical processes is a difficult problem. The first very extensive series of observations were made by *Favre* and *Silbermann*, about twenty-five years ago. Their results† will be marked F. S. in the following tables. At present, *J. Thomsen* (since 1853), at Copenhagen, and *Berthelot*, at Paris, are making the

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* The following simple cases may be mentioned here, in order to further elucidate the importance of the calorations recorded in the preceding articles.

Thus we have evidently, from 399—

$$H_2O+68.4\text{ gr.}^\circ=2H+O,$$

which reads: 1 mgr.at. water will give, upon the addition of 68.4 gr.°, 2 mgr.at. hydrogen and 1 mgr.at. oxygen. Again—

$$NCl_3=N+3Cl+16.2\text{ kgr.m.},$$

which reads: 1 milligram-atom of nitrogen chloride gives (upon explosion) 1 mgr.at. nitrogen gas and 3 mgr.at. chlorine gas, together with 16.2 kgr.m. of actual energy. Also—

$$N+3Cl+38\text{ gr.}^\circ=NCl_3;$$

that is: 1 mgr.at. nitrogen gas and 3 mgr.at. chlorine gas can be united, under the expenditure of 38 gr.°, to form 1 mgr.at. nitrogen chloride.

† The determinations by their so-called mercury-calorimeter are unreliable; but their results obtained by the water calorimeter are valuable, and here given.

most extensive and reliable determinations. When here reported, their values will be distinguished by Th. and B.

402. The method of experimentation is, when possible, that of mixture. The student may repeat some of the neutralization experiments (Chem. 150–152), by mixing 10 to 50 cc. of fifth-normal solutions in a small, light, glass flask, provided with a sensitive thermometer, indicating tenths of a degree. In this manner, the laws in regard to the atomicity of acids may be quite fully established. (See 430 to 435.)

403. In other cases, especially for combustions, a calorimeter with chamber is used (Chem. 46). The details of such experimental researches must be studied in special treatises on thermochemistry, and in the original papers of the above investigators.

404. We shall now give some of the more important results obtained by these investigators; and in this connection it must be stated, that not one of the many determinations thus far made permits the valuation of the caloration due to the simple chemical reaction in the process, because not even for gaseous substances have all the reductions involved been determined. (Compare 321, 322.)

Thus, one mgr.at. hydrogen gas and one mgr.at. chlorine gas give one mgr.at. hydrogen chloride gas and 22.0 gr.° (Th.); but how much of this caloration is due to the chemical combination, and how much to the changes of physical condition of many kinds, it is not yet possible to determine. Hence, it is absolntely necessary always to state sufficiently the physical circumstances*

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* The following estimates of *Berthelot* on this subject are interesting. The caloration gr.° due to the combination of two mgr.at. hydrogen gas and one mgr.at. oxygen gas at 0° is, according to the physical state (aggregation and temperature and pressure) of the water produced:

STATE.	TEMPERATURE.				
	—80°.	0°.	100°.	200°.	
Solid water (ice)	70.3	70.4	——	——	increases.
Liquid water	——	69.0	68.2	67.4	decreases.
Gaseous water (steam), when—					
(*a*) saturated (pressure variable)		58.1	58.6	59.0	increases.
(*b*) one atmosphere's pressure		——	58.6	58.8	increases.

under which the caloration was determined. Thus, in the above case we ought to write —

$$\text{H, gas} + \text{Cl, gas} = \text{HCl, gas} + 22.0\ \text{gr.}^\circ.$$

405. The combustion of a milligram-atom of carbon (12 mgr.) in its different conditions, gave (F. S.) in all cases a mgr.at. CO_2, gas, and —

for	charcoal	97.0	cal.
"	gas coke	96.5	"
"	graphite, artificial	93.6	"
"	graphite, native	93.1	"
"	diamond	93.2	"

Evidently, the 4 gr.° less obtained in the formation of the same CO_2 from diamond were consumed in the dissociation of the molecular combination. (Compare 77.) Indeed, we may calculate from this (by 400) that for a mgr.at. —

$$\text{C (charcoal)} = \text{C (diamond)} + 3.8\ \text{gr.}^\circ$$

In a like manner, the caloration of red and yellow phosphorus leads to the equation (see 63) —

$$\text{P (yellow)} = \text{P (red)} + 27.3\ \text{cal.}$$

406. Like differences prevail for dimorphous compounds. Thus, when a milligram-atom of the two native varieties of calcium carbonate (see Chem. pp. 141, 143) is dissolved in *dilute* hydrogen chloride, the caloration is (F. S.) —

$$1\ \text{mgr.at. } \textit{Calcite} + \text{HCl, aq} = \text{CaCl}^{\text{ide}}\text{, aq} + CO_2\text{, gas} + 4.6\ \text{cal.}$$
$$1\ \text{mgr.at. } \textit{Aragonite} + \text{HCl, aq} = \text{CaCl}^{\text{ide}}\text{, aq} + CO_2\text{, gas} + 6.0\ \text{cal.}$$

Consequently (by 400) —

$$1\ \text{mgr.at. } \textit{Aragonite} = 1\ \text{mgr.at. } \textit{Calcite} + 1.4\ \text{cal.}$$

In other words, calcite is the more stable form; hence it is found so much the more frequently. Besides, aragonite when heated suddenly falls to powder, which, under the microscope, exhibits the form of calcite (25).

407. The following table gives a few of the calorations due to the *synthesis* of the compounds mentioned, both compound and elements being in their ordinary condition (F. S). The units, as always in this work, are: mgr.at., gr.°, kgr.m.

SYNTHESIS OF 1 MGR.AT. COMPOUND.	PRODUCES		SYNTHESIS OF 1 MGR.AT. COMPOUND.	PRODUCES	
	gr.°.	kgr.m.		kgr.°.	kgrm.
H_2O	68.9	29.3	N_2O	—17.5	—7.4
Ag_2O	12.2	5.2	Cl_2O	—14.7	—6.3
CuO	43.8	18.6	Cl_2O_5	—130.5	—55.5
PbO	55.4	23.5			
FeO	68.9	29.3	*Chlorides.**		
ZnO	84.9	36.1	HCl	23.8	10.1
SnO_2	137.7	58.5	AgCl	34.8	14.8
As_2O_5	221.6	94.2	NaCl	94.9	40.3
As_2O_3	150.7	64.0	KaCl	101.0	42.9
P_2O_5	381.0	161.9	$CuCl_2$	59.0	25.1
P_2O_3	280.8	119.3	$PbCl_2$	89.5	38.0
P_2O	96.6	41.1	$FeCl_2$	99.3	42.2
SO_2	71.0	30.2	$ZnCl_2$	100.6	42.8
CO_2	96.0	40.8	$AsCl_3$	74.6	31.7
CO	29.7	12.6	$SbCl_3$	86.3	36.7

408. The results of determinations of the caloration of chemical synthesis here recorded indicate that the *affinity*, or *tendency to unite*, is, to some extent, measured by the caloration produced, or the energy equivalent thereto. Indeed, it may be said that the *energy producible by a chemical process is a measure of the affinities involved.*

409. Thus, the oxides which cannot be formed by direct synthesis exhibit a negative caloration, while the caloration for one atom of oxygen harmonizes very well with the readiness and energy of the chemical process of synthesis. The following gram-degrees represent, according to 407, the caloration produced by *one milligram-atom oxygen* in uniting with the elements mentioned:

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* Compare also NCl_3 of —38 gr.° (see 394).

Cl	—26.1 (5)	Cu	43.8	H	68.9
N	—17.5	As	44.3 (5)	Fe	68.9
Cl	—14.7 (1)	C	48.0 (2)	P	76.2 (5)
Ag	12.2	As	50.2 (3)	Zn	84.9
C	29.7 (1)	Pb	55.4	P	93.6 (5)
S	35.5	Sn	68.8 (2)	P	96.6 (1)

The numeral in the bracket indicates the number of oxygen atoms in one atom of the resulting compound, in case the same element unites in different proportions with oxygen (P, As, C, Cl).

410. A like series of values we obtain for the caloration produced by the synthesis of *one* milligram-atom of chlorine (see 407):

N	—12.7	Sb	28.8	Fe	49.6
——		Cu	29.5	Zn	50.3
H	23.8	Ag	34.8	Na	94.9
As	24.9	Pb	44.7	Ka	101.0

All of these elements, with the single exception of nitrogen, unite directly with chlorine, and the energy of the reaction is well expressed by the order of the elements in this series.

411. Nevertheless, it must not be forgotten that the caloration is an exceedingly complex quantity; hence the above series give not an exact representation of the order of their affinities (408 and 404).

It may suffice to call attention to the greatly varying caloration of the consecutive atoms of oxygen uniting with the same atom of the other element. Thus, the first atom of oxygen combining with one carbon atom produces a caloration of 29.7 gr.° per mgr.at. only; the second atom of oxygen produces 66.3 gr.°, because the caloration of CO_2 is 96.0 (see 407). If it were proper to assume that each each atom of oxygen uniting with the same carbon atom produces the same caloration y, we must suppose that the conversion of the carbon to a gaseous form requires a caloration x. Then we shall have $x+y=29.7$ and $x+2y=96$, from which $y=67.3$, the caloration for each oxygen atom uniting with a carbon atom, and $x=-38.3$. Hence, it would appear that the breaking loose of a carbon atom from its molecular combination in charcoal, and the conversion of the same atom to the gaseous form, requires an expenditure of 38.3 gr.° for every mgr.at. of carbon (equal to 12 mgr).

412. Only in two states do compounds appear under comparable physical conditions, so as to permit a closer and more direct estimation of the affinities (408) involved in a chemical process by the caloration of the same. These two conditions are the *gaseous* and *dilute aqueous solution* (one-fifth to one-tenth normal).

Under these circumstances, it does indeed appear that the affinity is measured by the caloration.

413. Hence we can predict, from the observation of certain calorations, the chemical reaction which must take place in other, but related, cases; for, let the synthesis $A + X$ give a caloration a, and the synthesis $B + X$ a caloration b — that is,

$$A+X=AX+a \qquad B+X=BX+b;$$

then, by the principle of 400, we shall have the equation—

$$A+B+X=AX+B+a=BX+A+b.$$

Hence, if a is greater than b, the process —

$$BX+A=AX+B+(a-b)$$

must take place, according to 412; while if b is greater than a, the reverse process —

$$AX+B=BX+A+(b-a)$$

will take place.

For example, according to the older determinations of Thomsen, the synthesis and solution —

$$R + Cl_2 + aq = RCl_2, aq + x$$

produces the following caloration, x:

mgr.at.	gr.°.	kgr.m.	mgr.at.	gr.°.	kgr.m.
R = 2 Ag	x = 22	or 9.4	R = Fe	x = 94	or 42.0
Cu	58	24.7	Zn	114	48.5
Pb	76	32.3	2 Na	203	86.3
2 H	78	43.2	2 Ka	208	88.4

414. Consequently, by 412, we obtain for R = Cu and Zn, by forming the equations for $Cu+Zn+Cl_2+aq$:

$$Cu+ZnCl_2,\ aq = Zn+CuCl_2,\ aq - 56$$
$$Zn+CuCl_2,\ aq = Cu+ZnCl_2,\ aq + 56$$

In words: Copper cannot substitute zinc in a dilute solution of zinc chloride, because the energy resulting from this process is a negative quantity. It would correspond to the lifting of a ton 23.8 mm. high for each mgr.at. of the metal used. But zinc will take the place of copper in the dilute solution of the latter, because the energy producing this process is positive, 56 gr.° for each mgr.at. zinc. In other words, when a mgr.at. zinc is thrown into a solution of copper chloride, there is mechanically a chance for a falling of a ton down 23.8 millimeters, or a kilogram down 23.8 meters. Now, since no kilogram weight ever refused falling when it reached a precipice of this height, the zinc never yet has refused to precipitate the copper under the above circumstances.

415. It cannot be doubted but that all chemical processes are regulated by the same law. *Chemical affinity* will, therefore, have to be considered as a simple, fixed force of attraction, comparable to gravity on the earth. The different magnitude of this affinity thus implies no occult properties in the elements, but merely indicates that they occupy different mechanical levels one towards the other, precisely as do the bodies on the surface of the earth.

416. Precisely as the same water on the surface of the earth will descend, by the force of gravity, from step to step down a series of cataracts, so will the same milligram-molecule of chlorine water ($Cl_2 + aq$) descend the *chlorine cataract of the elements** (Fig. 40, Plate II.), as each element in its turn is presented to the same; leaving each element free as the lower-level element is presented, precisely as the water leaves each step free as soon as the vertical gate at each brink, preventing its flow, is raised.

It is as absurd to ascribe the substitution of zinc for copper to an *electic affinity* between chlorine, zinc, and copper, as it would be to ascribe the flow of water to an electic affinity between the water and the higher and lower levels. It will undoubtedly have been noticed that this cataract of the elements corresponds to, and explains the order of, solubility, given in Chem. 174.

417. The same principle (400) may be used to indicate the apparently contradictory reactions familiar to the practical chemist. Thus, both in the dry and in the wet way, silver chloride is decomposed by hydrogen iodide; but, nevertheless, the silver iodide resulting is decomposed in a current of chlorine gas.

418. In order to apply the principle (400) to the reactions of the four elements, H, Cl, Io, Ag, in the presence or absence of water, we need only the following experimental data:

SYNTHESIS (MGR.AT.)		CALORATION (GR.°.).		
Hydrogen chloride,	HCl	......dry, 22.0;	wet, 39.3	(Th.)
Hydrogen iodide,	HIo	...... " —3.6;	" 15.0	(F.S.)
Silver chloride,	AgCl	...... " 34.8;	" 34.8	(F.S.)
Silver iodide,	AgIo	...... " 18.7;	" 18.7	(F.S.)

419. Consequently, in the *dry* way, the principle of 400 gives the equalities (gr.° for each mgr.at.)—

$$Ag+H+Cl+Io=AgCl+HIo+31.2=AgIo+HCl+40.7.$$

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* The steps must be the number of millimeters below the upper level (of the chlorine water sea) indicated by the figures of 413. Charts of this kind are quite instructive.

Hence, dry $AgCl^{ide}$ is decomposed by dry HIo^{ide}, under the caloration of $40.7 - 31.2 = 9.5$ gr.°, representing an energy of 4 kgr.m.

In the *wet* way, we have, in the same manner —

$$\begin{aligned} Ag + H + Cl + Io + Aqua &= AgCl,\ aq + HIo,\ aq + 49.0 \\ &= AgIo,\ aq + HCl,\ aq + 58.0 \end{aligned}$$

Consequently, $AgCl^{ide}$ will be decomposed in the presence of water by HIo^{ide} under the caloration of 9.0 gr.°, which represents an energy of 3.8 kgr.m per mgr.at.

420. But the reaction of gaseous chlorine on dry silver chloride is determined, by 400 and the synthesis calorations of 418, from —

$$Ag + Cl + Io = AgCl + Io + 34.8 = AgIo + Cl + 18.7,$$

which gives —

$$AgIo + Cl = AgCl + Io + 16.1,$$

which represents an energy of 6.4 kgr.m. tending to decompose the mgr.at. silver iodide by gaseous chlorine.

421. The following very interesting case we select from *Berthelot*, as an additional and very instructive direct demonstration of the general principles of 400. Let us take *equal volumes* of the following solutions, standarded* so as to contain equal atomicities in equal volumes:

Hydrates: $a = 2KaOH$, aq. $b = 2AmOH$, aq.
Acids: $x = 2HO_3N$, aq. $y = H_2O_4S$, aq.

Consequently, accordihg to 400, we must have —

$$a + b + x + y = M + k,$$

where M represents the *mixture* resulting, and k the total caloration obtained, which must be entirely independent of the *order* in which these liquids were mixed.

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* If a, b, x are fifth-normal, y tenth-normal, then 2 cc. of each will represent 2 mgr.at. hydrogen. The student may repeat the experiment with 20 cc. of each solution.

422. Now, this is confirmed by the determinations of *Berthelot.* The calorations (in gr.°) observed by him for each *mgr.at.* of a, b, x, y, were, in *two* entirely different courses:

I. Course.	II. Course.
$a + x \quad = a, x + 27.7$	$a + y \quad = a, y + 31.4$
$b + y \quad = b, y + 29.5$	$b + x \quad = b, x + 25.1$
$a, x + b, y = M \; - \; 0.2$	$a, y + b, x = M \; + \; 0.1$
Total, $k = 57.0$	Total, $k = 56.6$

The agreement of these two courses, each composed of three independently determined quantities, is as close as can be expected.

423. The same principle (400) is constantly used for the indirect determination of calorations which cannot readily be determined directly.

Thus, the caloration of the synthesis of methane, CH_4, has not yet been directly determined; but *Berthelot* has determined it, from the fact that a mgr.at. of CH_4, upon complete combustion to CO_2 and $2H_2O$, gives a caloration of 210 gr.° (F.S).

Let us put— $\quad C+4H = CH_4+x;$
hence— $\quad C+4H+4O = CH_4+x+4O.$

But, from experiments on actual combustion, these two sides become (using the numbers of *Berthelot*)—

$$CO_2+94+2(H_2O+69) = CO_2+2H_2O+210+x.$$

Hence, by reduction, $22 = x$; that is, the formation of one milligram-atom of methane gas from solid carbon and gaseous hydrogen produces a caloration of 22 gr.°.

424. It must be borne in mind, that *all* errors of the several quantities used will enter in the value thus indirectly determined. (Compare Induct. 31, 27; and School Laboratory, 1871, pp. 88–93.)

Let the error in the determination of the caloration of the synthesis of water be called w; the error in the caloration of the synthesis of carbon dioxide, c; and the error in the caloration of the combustion of methane, m; then the error, e, in the value of x will be, according to 423, $e = c + 2w - m$. If m have the opposite sign of c and w, tnen e may be quite considerable, while c, w, m each severally may not be large.*

425. The neglect of these rules of quantitative induction have already led to the introduction of a great many errors in the calorations reported by eminent experimentors.

426. The synthesis of the four typical compounds (151) is:

1. H, gas + Cl, gas = HCl, gas + 22.0 cal.
HCl, gas + Aq.† = HCl, aq + 17.7 cal.
hence: H, gas + Cl, gas + Aq. = HCl, aq + 39.3 cal.

2. 2H, gas + O, gas = H_2O, steam + 58.7 cal.
H_2O, steam + Aq. = 9.7 cal.;
hence: 2H, gas + O, gas + Aq. = H_2O, aq + 68.4 cal.

3. 3H, gas + N, gas = H_3N, gas + 26.7 cal.
H_3N, gas + Aq. = H_3N, aq + 8.4 cal.;
hence: 3H, gas + N, gas + Aq. = H_3N, aq + 35.1 cal.

4. 4H, gas + C (solid) = CH_4, gas + 22 cal.

Determinations 1, 2, and 3 are by *Thomsen*, while 4 is by *Berthelot*. (See 423, 424.)

427. The gradual synthesis of sal-ammoniac is thermically as follows (Thomsen):

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* According to *Thomsen's* accurate determinations, w = 0.6 for the determination (F. S.) used. This alone shows that the value, 22, above given is subject to an error of 1.2 gr.°, or 5 per cent.

† Aq. = aqua stands for *much* water—much in regard to the mgr.at. of the elements. Fifth-normal solutions are most convenient; they correspond to 275 mgr.at. water.

$3H$, gas + N, gas + Aq. = H_3N, aq + 35.1 cal. (See 408.)
H, gas + Cl, gas + Aq. = HCl, aq + 39.3 cal. (See 408.)
H_3N, aq + HCl, aq = NH_4Cl, aq + 12.3 cal.

Hence —

N, gas + $4H$, gas + Cl, gas + Aq. = NH_4Cl, aq + 86.7 cal.

But —

NH_4Cl, aq = NH_4Cl, solid + 3.9 cal.;

hence* —

N, gas + $4H$, gas + Cl, gas = NH_4Cl, solid + 82.8 cal.

This synthesis is graphically represented in Fig. 27, which again is given simply as a model for other syntheses.

428. The caloration produced by the synthesis of hydrogen sulphate (Chem. 133 to 135) has been accurately determined (by Thomsen) as follows, in gr.° for mgr.at.:

$2H$, gas + O, gas = H_2O, liquid + 68.4. (See 408.)
S, solid + $2O$, gas = SO_2, gas + 71.1.
H_2O, liq. + O, gas + SO_2, gas + Aq. = H_2O_4S, aq + 71.3.
H_2O_4S, liquid + Aq. = H_2O_4S, aq + 17.8.

Consequently (by 400) —

$2H$, gas + $4O$, gas + S, solid = H_2O_4S, liq + 193.0.
$2H$, gas + $4O$, gas + S, solid + Aq. = H_2O_4S, aq + 210.8.

The neutralization of this acid by potassium hydrate (Chem. 150 to 153) produces for one mgr.at. HS^{ate}, aq 31.3 gr.°; that is —

H_2O_4S, aq + $2KaOH$, aq = Ka_2O_4S, aq + 31.3. (Th.)

The additional water formed by the double decomposition involved need not be specially mentioned.

429. The following table contains the caloration determined by *Thomsen*, by the addition of n milligram-atoms of dilute sodium hydrate to *one* milligram-atom of the acid. His solutions contained the mgr.at. in 400 mgr.at. water—hence corresponded to $^{10}/_{72}$-normal. The results may, therefore, be verified by the student with fifth-normal solutions. (See 402.)

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* How much is the caloration of the solution of sal-ammoniac in water?

430. It will be noticed that the caloration increases with the number, n, of atoms of hydrate used, until n is 1, 2, 3, or 4—thereafter remaining practically unchanged, however much of the hydrate may be added. This characteristic phenomenon thus indicates, that the acids can neutralize either 1, 2, 3, or 4 atoms of the monatomic sodium hydrate; or, that *the acids are monatomic, diatomic, triatomic, or tetratomic.**

431. It will also be noticed that this thermally established atomicity agrees exactly with the chemical formula of the acid, being the same as the number of replaceable hydrogen atoms in the acid. (Compare 114.)

432. *Neutralization caloration* of the principal *acids*, as determined by *Thomsen* (1871):

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* Some prefer to speak of *monobasic*, etc., acids.

No.	ONE MGR.AT. OF ACID, aq,	PRODUCES, WITH n-MGR.AT. NaOH, aq, GR.° CALORATION, FOR n =						ATOMICITY OF ACID.
		½	1	2	3	4	6	
1	H-Cl	6.85	13.7	13.7	——	——	——	1
2	$H\text{-}O_3N$	6.8	13.7	13.7	——	——	——	1
3	$H\text{-}O_2C_2H_3$	6.6	13.2	13.2	——	——	——	1
4	$H\text{-}O_3P$	7.1	14.4	——	——	——	——	1
5	$H_2\text{-}O_4S$	7.1	14.6	31.0	——	31.0	——	2
6	$H_2\text{-}O_3S$	——	15.9	29.0	——	29.3	——	2
7	$H_2\text{-}O_4C_2$	6.9	13.8	28.3	——	28.5	——	2
8	$H_2\text{-}O_3C$	——	11.0	20.2	——	20.6	——	2
9	$H_2\text{-}O_3Si$	3.2	4.3	5.2	——	5.4	——	2
10	$H_2\text{-}HO_3P$	7.4	14.8	28.4	28.9	——	——	2
11	$H_3\text{-}O_4P$	7.3	14.8	27.1	34.0	——	35.3	3
12	$H_3\text{-}O_4As$	7.4	15.0	27.6	35.9	——	37.4	3
13	$H_4\text{-}O_7P_2$	——	14.4	28.6	——	52.7	54.5	4

Names of acids: 1, hydrochloric; 2, nitric; 3, acetic; 4, meta-phosphoric; 5, sulphuric; 6, sulphurous; 7, oxalic; 8, carbonic; 9, silicic; 10, phosphorous; 11, ortho-phosphoric; 12, arsenic; 13, pyro-phosphoric, or para-phosphoric.

Of additional acids, we give the neutralization caloration gr.° for one milligram-atom acid:

MONATOMIC.			DIATOMIC.		
Hydrocyanic,	H-Cy,	2.8	Chromic,	$H_2\text{-}O_4Cr$,	24.7
Sulphhydric,	H-SH,	7.7	Fluo-silicic,	$H_2\text{-}Fl_6Si$,	26.6
Hypophosphorous,	$H\text{-}H_2O_2P$,	15.2			

433. *Neutralization caloration* in gr.° for *one* milligram atomicity of different hydrates (*Thomsen*, 1871). If one atomicity of the positive be represented by π, one of the negative (element or compound radical) by ν, then the caloration given is x in—

$$\pi OH, aq + H\nu, aq = \pi\nu, aq + HOH, aq + x.$$

If the metal be n-valent, then $^1/_n$-mgr.at. will be required.

HYDRATE, CONTAINS	AMOUNT OF ACID.			HYDRATE, CONTAINS	AMOUNT OF ACID.		
	HCl	HO_3N	$\frac{1}{2}(H_2O_4S)$		HCl	HO_3N	$\frac{1}{2}(H_2O_4S)$
Li	13.85	——	15.65	½ Ni	11.30	——	13.05
Na	13.75	13.70	15.70	½ Co	10.50	——	12.35
Ka	13.75	13.75	15.65	½ $Fe^{(ous)}$	10.70	——	12.45
Tl	22.15	——	15.55	½ Cd	10.15	10.15	11.90
NEt_4	——	——	15.50	½ Zn	9.95	——	11.70
½ Ba	13.90	14.15	18.45	½ Cu	7.45	7.45	9.25
½ Sr	13.80	——	15.35	½ Pb	7.20	7.65	10.55
½ Ca	13.95	——	15.55	⅓ Al	9.30	——	10.50
½ Mg	13.85	13.75	15.60	⅓ Be	6.80	——	8.05
NH_3	12.25	12.30	14.10	⅓ Cr	6.85	——	8.20
NEt_3	12.50	——	14.15	⅓ Au	6.85	——	——
½ Mn	11.50	——	13.25	⅓ $Fe^{(ic)}$	5.60	5.60	5.65

434. It will be noticed that the crystalline precipitations: Ba, Pb, S^{ate}; Tl, Pb, Cl^{ide}, produce a greater caloration than the other neutralizations which do not give precipitates. This excess of caloration is evidently the latent heat of solution of these precipitates which is evolved upon solidification (Chem. 62).

435. The elements of which half an atom is thermally required for one HCl are diatomic; those of which one-third of an atom is required are, in their ic-compound, separately triatomic (98, 110). Hence, the thermal determination of atomicity agrees, also in the case of the electro-positives, with the simple, direct determination before given (96, 97).

436. The student should verify some of these neutralization calorations (429). If not, he ought at least to construct the *cataract* of hydrates for one of the acids (416), after having converted the gram-degrees into kilogram-meters or ton-millimeters. Besides, he ought to solve a number of *problems* involving the experimental data and the general principles of this section. The teacher should, of course, give these problems to the student.

437. It will have been noticed that the energy of neutralization of each atomicity is very nearly the same for the kaloid and calcoid hydrates, and that it is decidedly less for the heavy metals of the cadmoids and the siderous hydrates, while the least for the sideric hydrates. These thermal facts are, it will be recognized, in harmony with the chemical deportment of these substances.

438. Thus, the hydrates of the heavy cadmoids, also the siderous and sideric hydrates, are replaced by the hydrates of the kaloids and calcoids with a degree of energy indirectly (by 400) given in the table of 433. (See 417 to 420.)

For example:

$$2(NaOH, aq) + Cu(OH)_2, aq + H_2O_4S, aq =$$
$$= Na_2O_4S, aq + Cu(O_4H)_2, aq + 2(HOH, aq) + 31.4.$$
$$= 2(NaOH, aq) + CuO_4S, aq + 2(HOH, aq) + 18.5.$$

Consequently, the CuS^{ate} solution is decomposed by NaH^{ate} with an energy of 12.9 gr.°, or 5.48 kgr.m.

439. Calculate the energy of a number of such decompositions; also the energy of the solution of the resulting hydrates in any of the acids of 432.

440. The caloration of the reactions of serials has not yet been very extensively investigated. *Berthelot* has, however, made numerous determinations. Since no very important general results have thus far been obtained, it may here be sufficient to give a few of the calorations of the complete *combustion* of serials (mostly determined by F. S).

	AMOUNT OF SUBSTANCE BURNT.	CALORATION, GR.°.	
		1 mgr.	1 mgr.at.
Methane	CH_4	——	210
Ethylene	C_2H_4	——	334
Amylene	C_5H_{10}	11.5	804
Cetene	$C_{16}H_{32}$	11.1	2476
Turpentine oil	$C_{10}H_{16}$	10.9	1476
Acetone	C_3H_6O	7.3	424
Methylalcohol	CH_4O	5.3	170
Ethylalcohol	C_2H_6O	7.2	330
Amylalcohol	$C_5H_{12}O$	9.0	788
Cetylalcohol	$C_{16}H_{32}O$	——	2565
Formic acid	CH_2O_2	——	96
Acetic acid	$C_2H_4O_2$	3.5	210
Butyric acid	$C_4H_8O_2$	5.6	497
Valerianic acid	$C_5H_{10}O_2$	6.4	657
Palmitic acid	$C_{16}H_{32}O_2$	9.3	2385
Ethyl ether	$C_4H_{10}O$	9.0	668
Amyl ether	$C_{10}H_{22}O$	10.2	1610
Methyl formate	$C_2H_4O_2$	4.2	252
Methyl acetate	$C_3H_6O_2$	5.3	395
Methyl butyrate	$C_5H_{10}O_2$	6.8	694
Methyl valerate	$C_6H_{12}O_2$	7.4	856
Ethyl formate	$C_3H_6O_2$	5.3	391
Ethyl acetate	$C_4H_8O_2$	6.3	554
Ethyl butyrate	$C_6H_{12}O_2$	7.1	823
Ethyl valerate	$C_7H_{14}O_2$	——	1018
Amyl valerate	$C_{10}H_{20}O_2$	——	1469
Cetyl palmitate*	$C_{32}H_{64}O_2$	10.3	4964

441. If we, with *Berthelot*, consider the caloration of one mgr.at. gaseous CO_2 from solid pure carbon and gaseous oxygen to be 94 gr.°, and the caloration of the synthesis of one mgr.at. water 69 gr.°, then we can, from the above values (440), calculate the caloration due to the synthesis of these serial compounds. The process has been exemplified already (423).

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* Spermaceti.

The student should work a number of these problems. Compare the results for isomeric bodies.

442. The caloration produced by the combustion of complex serials has been determined by *Frankland* (1866) on account of the physiological interest of this caloration. (See Cosmical Chemistry.) Here we report only a few of his results. The caloration *C*gr.° due to *one milligram* of the substance mentioned in its common condition, *i. e.*, with *a* per cent of water is:

CARBONACOUS FOOD.	a.	C.	NITROGENOUS FOOD.	a.	C.
Carrots...........	86	0.5	Milk	87	0.7
Apples	82	0.7	Eggs, white.....	86	0.7
Potatoes..........	73	1.0	" yolk	47	3.4
Bread, crumb...	44	2.2	Veal	71	1.3
" crust.....	—	4.5	Beef..............	71	1.6
Sugar	—	3.3	Ham	55	2.0
Butter............	—	7.3	Cheese...........	24	4.6
Tallow	—	9.1	(Cod liver oil...	—	9.1)

443. These calorations represent also the energy expended in the formation of these products from CO_2, H_2O, and N of the atmosphere — an energy ultimately derived from the sun.

In the annimal organism, the combustion is slow and gradual. Carbonaceous food may be completely burnt to CO_2 and H_2O by the system; but nitrogenous food never yields nitrogen gas in addition, but *urea* (see 194), which, by combustion, gives 2.2 gr.° for each mgr.*

444. The caloration due to the mixture of liquids, the absorption of gases by liquids and gases, and the solution of solids in liquids, ought also here to be considered; but, thus far, hardly any general principles have been disclosed by the study of the multitude of facts. Besides, many of these "facts," resting exclusively on the use of the mercury-calorimeter, are themselves far from reliable. (See 401.)

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* Since now, for example, the dry white of eggs yields one-third of its weight of urea in the organism, one mgr. of ordinary white of eggs gives about one-twentieth of a milligram of urea; so that in the organism, at most, 0.6 gr.° can be realized rom each milligram of whiteof eggs.

445. The most accurately determined caloration of this kind is the mixture of *sulphuric acid* with water. *Thomsen* finds that one mgr.at. H_2O_4S, when mixed with n mgr.at. H_2O, produces the caloration $^{18}/_{k}$ gr.°, where $k = 1 + \frac{1.862}{n}$. It gives, therefore, with 1, 2, 3, ... 1,000 atoms of water, respectively: 6.3, 9.3, 11.1, ... 18.0 gr.°.

446. The solution of one milligram of the following solids and gases produces the caloration here given:

1 mgr.	nitre,	at 6° C, in 20 mgr. water,	−0.086	gr.°
1 "	common salt,	10° C, " 7 " "	−0.015	"
1 "	hydrogen chloride,	in much water,	+0.45	"
1 "	sulphur dioxide,	" " "	+0.12	"
1 "	ammonia,	" " "	+0.51	"

447. The most general result from the facts and principles of caloration exposed in this section is this: *Chemical affinity is not an occult force.* To speak of elective affinity, predisposing affinity, etc., etc., as has been done by "metaphysicated" chemists of the old school, is simply absurd.

Under given conditions, the atoms of the various elements and compounds unite or separate, exactly as larger masses move when subjected to given mechanical conditions. *Not only the total weight, but also the total energy* (actual and potential, see 397), *remains constant under all processes* — not less in the mutual actions of atoms in chemical processes, than in the mechanical phenomena of the most elementary machines. (Phys. 450.)

448. The search for the *velocity* of chemical actions, as something peculiar, is therefore also futile. *The velocity of chemical processes must, in its general features, be determined by the law of probability*, precisely as we already have shown this law to govern the chemical process of dissociation, and as it is known to govern the process of ebullition; for all these actions really relate to the fate of individuals (here atoms) in a great multitude of individuals (here a mass), while this latter is acted upon in a given manner. By simply drawing balls from an urn containing white and black balls of equal size, these laws may be established. (See 367, 374 to 377.)

449. The simplest experimental determination of the velocity of a chemical process consists in the measurement of the volume of gas produced. The number of such processes is quite considerable: the dissolution of solids in dilute acids (Chem. 172, and 190 to 193), the dissociation of solid compounds at a given temperature (Am N^{ate}, 104; also, Chem. 100, 141), or any reaction by which, from two limited masses, a gas is evolved (for example, a urea solution gently warmed with Millon's reagent*).

These experiments may be performed by means of our gas-burette (56), or by simply collecting the gases in a graduated test-tube inverted over water.

450. Take, for example, about 3 mgr.at. zinc in 30 cc. dilute acid containing about one-third its volume of hydrogen chloride; consequently, about 3 mgr. molecules (between 60 and 80 cc., according to pressure and temperature) of hydrogen will be evolved in a few minutes. Read off the volume every fifteen or twenty seconds; record the results. Reduce volumes to per cent of the entire volume; construct the curve of these amounts, S; find the velocity, v, per minute in the same manner as in 366 to 377, and compare these observed values to those (v′) which correspond to the law of probability. The agreement between observation and calculation will be found quite satisfactory,* so that *the velocity of such chemical processes is indeed determined by the law of probability.* (*Hinrichs.*)

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* Millon's reagent is prepared by dissolving 1 part of metallic mercury in 1⅓ of strong nitric acid (specific gravity, 1.40), first in the cold, thereafter completing the dissolution by moderate warming. One volume of the solution is diluted with water to form three volumes.

The above reaction is: one atom of urea = NH_2-CO-NH_2 with O from the reagent, gives one molecule of nitrogen gas, N_2, one molecule of carbon dioxide gas, CO_2, and two molecules of water, which remain in the flask. (See 194.)

Section XVII. Crystallization.

451. The *crystal form* of a compound is one of its most essential properties. Hence, it has already been studied in general (Phys., Chap. III., Sec. V.), and also with special reference to its degree of *symmetry* (Chem. pp. 233 and 234). The application of the crystal form as characteristic quality is exemplified in our description of the principal minerals (Chem. pp. 129–155; see, also,

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* *P. Waage* and *C. M. Guldberg*, in their very important *Etudes les sur Affinites Chimiques*, Christiania, 1867, have given a great number of such series of observations; but it does not seem that they are aware that the law which they seek is as stated above. Hence, we may give their series 10, page 29, as an example.

At 6.8 minutes, fifty per cent of hydrogen had been evolved from zinc-wire and HCl. This point is, therefore, taken as the middle of the process, or $n = o$. Consequently, $n = 2$ corresponds to 8.8 minutes, $n = -3$ to 3.8 minutes, etc. Carefully constructing their forty-one observations, we obtain our curve S, from which we find the *observed* velocities, v (per cent of total gas), at the instants, n. We find, thereafter, that in this case the probability curve is determined by—

$$\log v' = 1.19 - 0.03 . n^2,$$

which represents the observed values with the errors $e = v - v'$, as follows:

n =	−5	−4	−3	−2	−1	0	1	2	3	4	5
v =	2	5	9	11	14.5	15.0	15.5	13	10	3	1
v′ =	2.8	5.1	8.3	11.8	14.5	15.5	14.5	11.8	8.3	5.1	2.8
e =	−0.8	−0.1	0.7	−0.8	0.0	−0.5	1.0	1.2	1.7	−1.9	−1.8

The concordance is most admirable for the first half of the process; for the latter half, the observed velocity is at first ($n = 1$ to 3) too great, the zinc evidently having become porous, thus giving its solution a *greater than an even chance.* As a matter of course, the last observations ($n = 4, 5$) fall correspondingly short. Construct these curves.

24 and 24*). In fact, the crystal form is for solids as important a physical character, as the boiling point for volatile liquids (Sec. XIV.)

452. The importance of crystal form to theoretical chemistry is still enhanced by the fact that other physical properties of any given substance are most remarkably modified by crystallization. Thus, *cleavage* is determined by the crystal form (25, 26; Phys. 197, 198); the *hardness* varies from face to face (Chem. pp. 148, 149, cyanite); *electricity* (Chem. p. 150, turmaline), and even *magnetism* (Chem. p. 149, cyanite), is dependent on the crystal form. But most striking and most readily observed is the influence of crystal form on *light.* (See note on p. 47; also, arts. 405, 405, and Phys. 288 to 296.)

453. In fact, the crystal form simply is the outward evidence of the most intimate *structure* of the crystal itself. Hence, various attempts have been made to deduce the crystal form from the chemical constitution of the substance.

The first *simply mechanical deduction of the crystal form from the chemical composition of the substance* was published in 1867, in our *Atomechanik.** Here it will be sufficient to indicate this mechanical theory of crystal structure in general. For further details, we must refer to numerous publications of ours on this subject. It is necessary, however, to first explain the terms of *isomorphism* and *dimorphisms*, and the fallaceous reasonings, which have been based thereupon.

454. One and the same chemical substance is said to be *dimorphous,* if it exists in two distinct crystal forms (see calcite and aragonite, Chem. pp. 141–143); if in three, it is *trimorphous* (see TiO_2, Chem. p. 138, Nos. 4, 5, 6); if in more, *polymorphous.*

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* The constructions of *Gaudin* conflict with mechanical principles. The calculations of *Schrauf* rest upon the untangible magnitude which he calls the "*optical equivalent.*" *Knop's* experiments on the growth of crystals have also some bearing on this subject.

Several months before the publication of the *Atomechanik*, the author communicated the law of 463, and its application (464 to 468) to the anhydrous carbonates, to *J. D. Dana*, editor of the *American Journal of Science*. Soon after the publication of the *Atomechanik*, the same editor published in his journal a hasty and unwarranted generalization of my views, as his own independent discovery.

455. But it can be demonstrated* that no substance exists in two or more absolutely different forms. On the contrary, the different forms exhibited by so-called polymorphous substances are very closely related to one another, being simply different forms of equilibrium of the same molecule.

456. Different substances are said to be *isomorphous,* when they have the same crystal form, very nearly. (Compare Phys. 183, and 194 to to 196.) If the forms closely resemble one another, without being very nearly the same in angular dimensions, they are termed *homœomorphous.*

457. For remarkable isomorphous groups, see 122 and 123. Other instances will be found in descriptive mineralogy: the isomorphous *calcite-group* (Ca, Mg, Zn, Mn, Fe, carbonate, Chem. pp. 141–142); the *aragonite-group* (Ca, Sr, Ba, Pb, carbonate, Chem. p. 143); the *barite-group* (Sr, Ba, Pb, sulphate, Chem. p. 138); the *spinel-group* (Chem. p. 137, embracing 81, 2, 3; 82, 1; 84, 1); the *hematite-group* (Chem. p. 135, 64, 1 and 2); and many others.

458. In all of these cases, the chemical formula is the same in general for each group, only *one* element-atom being different from one substance to the other. Thus, the calcite group is represented by the formula RO_3C, wherein R may be Ca, Mg, Zn, Mn, Fe singly, or several of these elements in varying proportions.

459. One of the most stupendous "logical" inferences has been drawn from such facts—namely, that the varying (*vicariating*) elements are themselves isomorphous.

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* *Atomechanik,* Section IV.

Even a classification of the elements has been based upon this conclusion. (See *Graham's* great work on chemistry.)

But it is evident that the near equality of the crystal form of CaO_3C and MgO_3C does not prove anything whatever in regard to the crystal form of the metals Ca and Mg; for they enter only as one atom each in a structure of five.

460. If we bear in mind the definition of a molecule (41), and the fact that the atoms of the same are at relatively great distances from one another (163, 158; Fig. 4), then it will be almost incredible that the above inference (459) ever was drawn. For it will then be evident that, *whatever* be the magnitude and form of the individual atoms, the form of the molecule, depending only on the co-ordinates of these atoms, will remain the same so long as the chemical constitution is the same. Hence, if the form of the molecule determines the form of the crystal (26), it follows, that *compounds of the same chemical constitution must be isomorphous*, or, rather, homœomorphous.

461. Hence, not only all carbonates of the formula RO_3C (see 459), but all compounds of the general formula AB_3C, *must be isomorphous*, irrespective of any special properties (form, weight,) of the atoms, which special properties can only produce small changes, called *crystallographic perturbations*, from a certain mean form.

462. This is fully confirmed by the great group of isomorphs, of which the following represents a few cases:

FORMULA.	NAME.	RHOMBOHEDRON OF	
AgS_3Sb......	Pyrargyrite..............	108.7°	Chem. p. 138.
NaO_3N.......	Nitratite	106.5°	Chem. p. 140.
CaO_3C.......	Calcite.....................	105.1°	Chem. p. 141.
(KaO_3Cl......	Potassium chlorate....	104.4°, 105.6° ..	Phys. 179.)

The dimorphism in this group is only apparent (see 455).

463. The degree of symmetry (Chem. p. 126) of the compound AB_3C may be theoretically determined in the following manner:

The three atoms B, being equal material particles, can, when alone, only have one position of stable equilibrium — that of an *equilateral triangle* (Fig. 28, a). Whatever be the position and nature of the other two atoms, A and C, they can only produce some slight changes in this position. Such slight changes we have termed *crystallographic perturbations* (461).

464. It is evident that from equilateral triangles only *rhombohedral* and *hexagonal* forms can be constructed. (Compare Chem. p. 126.) This is geometrically indicated in Fig. 28, b, c. The corresponding crystal forms are *hexagonal prisms* of 120°, *hexagonal pyramids*, *rhombohedræ*, *scalenohedræ* (see Chem. p. 133, quartz; p. 135, hæmatites; p. 141, calcites; etc.); and also the *rhombotesseral forms* — that is, any of the tesseral forms in the so-called *rhombohedral position*, which corresponds to the octahedron resting on one of its faces. (Chem. p. 128; Phys. 191. See the tabular forms of alum crystals.)

In general, *all compounds expressible by the general formula* AB_3C *must crystallize in forms which have rotary symmetry of* 120° *or* 60° — or have forms deviating but slightly from such.

465. It must be borne in mind that a crystal has rotary symmetry of 120° when, after a rotation of 120° around an axis, it coincides exactly with its former position — that is, all faces occur *in groups of three equal faces around the axis of rotation*. Any such three equal faces constitute one-half of a *rhombohedron* of the number of degrees equal to the interfacial angle of the faces. Thus, the dedecahedron in its rhombohedral position exhibits the rhombohedron of 120°; the hexahedron (cube), a rhombohedron of 90°. (Phys. 190.)

466. Thus, the calcite group of the carbonates, is *exactly* hexagonal (see 462). The members of the aragonite group differ slightly from this (see 464), since the vertical prism differs from 120° by the following amounts:

Witherite	Ba	—1.5°;
Strontianite	Sr	—2.7°;
Aragonite	Ca	—3.8°;
Cerusite	Pb	—2.8°.

It will easily be seen that the perturbation of the triangle itself is only one-half as great as the above perturbation of the angle of the vertical prism.* (See Fig. 28, c.)

467. If the preceding deductions in regard to the form of crystals of AB_3C be correct, it follows that all more complex compounds, which may be chemically represented by this general formula, also are of rotary symmetry of 120° or 60° (see 464, 465), or nearly so. Hence, the great number of chloroid ternaries indicated in 122 must have this form, for if we represent the titanoid by $\mathrm{T}\tau$, the chloroid by X, the compounds in question can be written —

$$R''(X_2 + 2aq)_3\mathrm{T}\tau, \quad \text{and} \quad R''(X_2 + 4aq)_3\mathrm{T}\tau,$$

which formulæ are of the form AB_3C.

This conclusion is confirmed by the beautiful crystallizations of these compounds. *Marignac*, *Bonsdorff*, and *Topsoe* have indeed found that these compounds are rhombohedral in their crystal form.

468. The anhydrous chloroid ternaries of 116, 117, and 118 are represented by the same formula, AB_3C, if A is a diatomic element, $B = Cl_2$ or Br_2 or Io_2, and $C = Pt$, Pd, Ir, or Cd. The form is *tesseral* in the rhombohedral position, which is therefore explained by the above theory. (Compare 463.)

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*For details on molecular perturbations of crystals, see No. 3 of my Contributions to Molecular Science, 1870.

469. The position of the atoms A and C in the compound AB_3C, of which the equilateral triangle formed by the three atoms B has thus far been considered, can also be determined; for the two atoms necessarily determine a straight line, which can only be either parallel or at right angles to the triangle 3B.

Since each atom B has a tendency to combine with A and with C, we consider the second position the true one; so that Fig. 29 gives an axonometric drawing of the molecule AB_3C. We call the plane BB′B″ the *equator*, and the line AC the *axis*, of the molecule.

470. The angle ABC we have (in the *Atomechanik*) demonstrated to be a right angle if B is a single atom — that is, AD = BD = CD. *The corresponding form is a rhombohedron of* 104.5° ($104^1/_2$).

From this *normal* crystal form the *actual* crystals can differ only by small values, the molecular perturbations, due to special secondary actions of the elements in each given case (461, 462).

471. The following *table* gives the observed values of the rhombohedral angle, R; the *perturbation* of the same, p — that is —

$$R = 104.5 + p$$

also, a reference to the page of our *Elements of Chemistry* where the observed form is described:

FORMULA.	NAME.	R, *Degrees.*	p, *Degrees.*	PAGE.
AB_3C	Normal deltoid	104.5	0.0	—
CaO_3C	Calcite	105.1	0.6	141
NaO_3N	Nitratite	106.5	2.0	140
MnO_3C	Rhodochrosite	106.9	2.4	142
FeO_3C	Siderite	107.0	2.5	142
MgO_3C	Magnesite	107.5	3.0	142
ZnO_3C	Smithsonite	107.7	3.2	142
AgS_3As	Proustite	107.8	3.3	133
AgS_3Sb	Pyrargyrite	108.7	4.2	133

472. The perturbations are all positive — that is, the rhombohedræ observed are all *more obtuse* than the normal or theoretical rhombohedron of 104.5°. In other words, the vertical axis AC of Fig. 29 is *shorter*, indicating an attraction between A and C greater than in the equator between B and B′.

This is also theoretically foreseen, for $2O = 32$, but the mass $Ca + C = 40 + 12 = 52$ is greater. Also, in the last two sulpho-salts, $2S = 64$, but $Ag + As = 108 + 75 = 183$ and $Ag + Sb = 230$ is much greater.

473. In this connection, it is important to observe that calcite expands in the direction AB, while it contracts in the equatorial direction (Fig. 29), when heated — that is, its rhombohedral angle *diminishes* upon heating (Chem. 40). Consequently, the increasing of the temperature of calcite, *diminishes* its perturbation 0.6 degrees (or 36 minutes). At 164° C, the rhombohedron of calcite is only 104.8 degrees, while at 10° it is 105.1 degrees. Accordingly, at about 300° C, the perturbation will have been reduced to zero — that is, at the temperature at which calcite begins to dissociate, or where its special attractions are in equilibrium with the caloric vibrations (see 380). This confirmation of the theoretically determined crystal form of calcite is very important.

474. The compounds represented by the general formula AB_4C have a quadratic equator formed of the four atoms B and the axis AC (see Fig. 30) equal to the diagonal of the equator. This general form is modified in case a proximate constituent of different form enters (as in the case of the sulphates).

The crystal form resulting from the above is evidently tesseral — Fig. 30 really represents an octahedron (Phys. 190).

475. This accounts for the crystal form of the *spinel-group*, which embraces the following minerals: spinel, gahnite, chromite, magnetite, and others (Chem. p. 137).

The form of the alums is also explained hereby, because their general formula (123, b,) may be written AB_4C, if $A = Ka_2$ $C = \Sigma\iota_2$, and $B = O_4S + 6$ aq.

476. The theoretical determination of the crystal form of the great number of compounds which may be represented by the chemical formula AB_2 is of especial importance; for some of the most common crystallized substances are represented by this formula, such as the *snow-stars*, H_2O, the crystals of *quartz*, SiO_2, the crystals of *pyrite*, FeS_2, and the crystals of *fluorite*, $CaFl_2$. These forms are. at first sight, very different from one another, thus increasing the difficulty of the solution of the problem.

477. The three atoms of AB_2 being at distances from one another which are great in comparison to their own dimensions, they may be considered, in a first approximation, as three material points. Consequently, they mark the corners of a triangle, the straight line being impossible, because unstable. But since the atoms B are equal, they must sustain the same relation to A; hence, the triangle (Fig. 31) is iscoceles, BB′ being the base, and the atom A marking the vertex.

478. If there were no special differences at all between A and B, the triangle would evidently be equilateral. Hence, *the form of the molecule or compound atom* AB_2 *is an equilateral triangle*, as first approximation; but the form may differ from this by certain small *molecular perturbations*, determined by the differences between the atoms A and B.

479. Consequently (compare 462 to 465), *the crystal form of the compounds of* AB_2 *has rotary symmetry of* 60° *or* 120° — *i. e.*, is *rhombotesseral*, *rhombohedral*, or *hexagonal* —more or less nearly.

How the vertical axis of the crystal can be determined, is shown in special treatises (see *Atomechanik*).

480. This theoretical result is fully confirmed by the observed crystal form of the compounds of the formula AB_2. Thus, we have:

a. RHOMBOTESSERAL, the *pyrite-group*, namely: *pyrite*, FeS_2 (Chem. p. 130); *cuprite*, Cu_2O (p. 136); *argentite*, Ag_2S (p. 132); *fluorite*, $CaFl_2$ (p. 153).

b. HEXAGONAL, the *quartz-group*, namely: *quartz*, SiO_2 (Chem. p. 133); *water*, H_2O (p. 136, in the beautiful snow stars); *lead iodide*, $PbIo_2$ (see p. 9 of this volume).

c. NEARLY HEXAGONAL, the basal angle of the triangle differing from 60° by the *perturbation*,*. the amount of which is stated in degrees and tenths of a degree: *cassiterite*, SnO_2, —3.9° (Chem. p. 134); *rutile*, TiO_2, —2.8° (p. 135); *marcasite*, FeS_2, —0.5° (p. 131).

481. The best artificial crystals of this kind are those of lead iodide, $PbIo_2$, formed and observed as directed (on p. 9 of this volume). The most valuable for careful study are those of quartz and fluorite. But the most abundant and delicate are those of water, in the *snow star.* By observing the form of the snow stars during a cold but not abundant fall of snow, as they rest upon the dark woolen garments, you will be surprised by the variety of detail in the delicate beauty of form of the always six-sided snow stars. Many hundreds of slightly differing star forms have been observed — but all *hexagonal* — all elements of the stars constructed by the repetition of the angle of sixty degrees.

482. It is therefore worth while to show how these forms arise from the water-atom, the form of which is represented in the equilateral triangle (see 478), especially as this will give us an opportunity to show how crystals grow in general.

The facts of cleavage (see 25, 26,) demonstrate that *a crystal is composed of its molecules in exactly parallel positions.* As the molecules one after another separate from the gas or solution, they cease their rotations (308), and remain *fixed* in positions *parallel* to that of the crystal already existing. This is the *general law of aggregation*, or *crystallization.*

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* A negative perturbation indicates attraction, shortening of the height of the triangle (Fig. 31).

483. It is evident that the formation of a serial molecule is similar to this process of crystallization (compare 157, 158). Indeed, the synthesis of a serial molecule may be considered the parallel *aggregation of atoms*, exactly as the crystallization is the parallel *aggregation of molecules.*

484. Now, by the aggregation of equilateral triangles (molecules of water, H_2O), the various snow stars are built up as exemplified in Fig. 32. It will be noticed that the molecules throughout the crystal are parallel. Since now any of these molecules again may become the center of a new star, the pennate forms so frequent among the snow stars are explained (Fig. 33).

485. The formation of different, but related, forms, on one and the same crystal, has long ago been fully explained by the laws of aggregation. Thus, if the *rate of growth* be equal in the three rectangular directions of the axis in Fig. 34, an *octahedron* will evidently result; but if the rate be different according to the different axes, other crystal forms will result, the aggregation and the crystal molecules remaining the same. (Compare Phys. 190; Chem. 234.)

486. If, in general, the progress in the three directions, X, Y, Z, be h, k, l times the inter-molecular distance—that is, if in the direction of the axis X, h molecules are added by growth, while in the direction of Y there are added k molecules, and in the direction of Z, l molecules are added—the *secondary form*, denoted by hkl, will arise. Of course, *the simpler these figures* h, k, l, *the more frequent the corresponding faces.*

This is strikingly confirmed by the actually observed faces of crystals, as is shown in special treatises on crystallography. (See *Hinrichs' Principles of Pure Crystallography*, 1871, p. 31.)

487. This apparent *selection* of the simplest forms in the act of crystallization is not the only selection manifested in the growth of crystals; for if we, on the basis of complete enumeration of all observed crystal forms, arrange these according to their *degree of symmetry* (Chem. 233), we find that the higher degrees of symmetry prevail over the lower ones. But, since the number of possible forms of lower symmetry is much greater, *matter in the act of crystallization seems to select the forms of higher symmetry.*

488. Thus, of 1,944 measured crystallized substances, 94 only have no symmetry (*triclinic*), 571 have one plane of symmetry (are *monoclinic*), and 1,279 have two (three) planes of symmetry (are *orthoclinic*). Of these latter, 538 have no rotary symmetry (are *rhombic*), while 741 have rotary symmetry (are *quadratic*, *hexagonal*, *rhombohedral*, or *tesseral**).

489. The cause of the selection of the simpler secondary forms is the exact *parallelism* of the molecules in the crystal. The cause of the *selection of the higher forms of symmetry* is the *simple normal form of the chemical types*, which again are the *mechanical consequences of the law of simple multiple atomic proportions.* This we shall show in as concise a manner as possible.

490. The *simple chemical types*, expressive of the law of simple multiple atomic proportions (see 38, 39), are, for *binaries* (see 45 to 48, 91 to 93)—

$$AC \qquad AC_2 \qquad AC_3 \qquad AC_4$$

and for *ternaries*, one, two, three, or four atoms of an intermediate element, B, added to either of the above binaries. Since now this intermediate element unites separately with A and C, we write it between the two (see **114** to **120**, also **469**); for example —

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* For additional details, see my paper on the "Statistics of Crystal Symmetry," in the Proceedings of the Academy of Vienna, 1870; also, our "Principles of Pure Crystallography."

ABC AB_2C AB_3C AB_4C

491. The mechanical constitution of these types is already deduced in preceding articles of this section, at least indirectly, as represented in Fig. 35. First, AC (Fig. 35, a,) necessarily forms simply a straight line. In AC_2, the atoms C necessarily form a straight line — their center of gravity is D, exactly in the middle of this line, and the line from the atom A to this center of gravity is perpendicular to the line CC. (Compare 477, 478.) The type AC_3 (Fig. 35, c,) differs simply by B_3 forming an equilateral triangle (see 462), of which D is the center of gravity, and to which AD is perpendicular. In the type AC_4, the four atoms C form a quadrilateral, of which D is the center of gravity, and to which again AD is perpendicular (Fig. 35, d). It is easily seen how A_2, A_3, etc., will modify this form.

492. Now take this line AD as *axis*, and let E indicate a plane at right angles to AD; then this plane will be the *equator* of the molecule, and the *place* of the atoms B in the ternaries (Fig. 35, e). In ABC, of course only *one* atom will be in this plane. In AB_2C, the two atoms B will be at opposite extremities of the same diameter (Fig. 35, f). In AB_3C, the three atoms B will form an equilateral triangle (Fig. 35, g; see 262 to 269). In AB_4C, the four atoms B will form a quadrilateral (Fig. 35, h).

493. There are, of course, simply the *normal forms*, from which the *actual forms* will differ by certain small quantities or *perturbations*, the values of which are determined from the special nature of the constituent atoms in each case. Thus, the perturbations, p, of the normal prism of 120° in the carbonates of the aragonite group is, in degrees —

$$p = \frac{24}{1000}(Xa - 200) \text{ degrees.}$$

This formula gives, for Ca, Sr, Br, values which exactly coincide with those observed (see 466).

494. Of the more complex salts of inorganic chemistry proper, it may be sufficient here to represent the pyro-salts (or para-salts) $A_4B_7C_2$, where, for $B = O$, we have, if C is: P, pyrophosphate; As, pyroarsenate; Bo, tetraborate; Cr, bichromate; and for $B = S$ we have, if C is: As, sulphobiarsenate; Sb, sulphobistibate; Fe, sulphodiferrate. (See 114 and 115.)

Fig. 36, b, shows the constitution of sodium pyrophosphate, $Na_4O_7P_2$, as it results by the union of two atoms of common sodium phosphate, Na_2HO_4P, under the loss of one atom of water.*

The water of crystallization apparently is largely distributed in the equator of the molecule (compare 467).

495. It is believed that this section gives sufficient details in regard to the constitution of crystals, so that the general student (see 4) may understand that the problem of the determination of the crystal from the chemical constitution is solved in a great many of the most important cases.

For more special information on this very important subject, we must refer to special memoirs and treatises. This is equally necessary in regard to the relation of *molecular volume* to crystal form, and many other properties (especially optical and electrical) of crystals.

Section XVIII. The Element-Atom an Atom-Crystal.

496. The *crystal* has been found to be the parallel aggregation of molecules (482). But the molecule is a similar aggregation of the element-atoms (see 483). What is the element-atom? Is it not, itself, the aggregation of atoms of a primary matter, *the* matter?

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* The common phosphate crystallizes with twelve atoms of water. By heat, it loses this water of crystallization, and also the above water, by dissociation. The pyrophosphate crystallizes well from concentrated aqueous solutions.

497. This question admits evidently of *two* solutions — the theoretical and the experimental. The latter, *the actual decomposition of all elements into one substance*, has, so far, not yet been furnished (Chem. 96), although, in the past history of chemistry, quite frequently substances have been proved to be compounds that were held to be elements. Whether this experimental demonstration of the composite nature of the elements will be furnished soon, is a matter of uncertainty. It is, however, much more likely to be furnished than not, on account of the first (the *theoretical*) answer to the above question, for, as theoretical chemistry has progressed, its answer has become more and more positive, affirming the composite nature of the chemical elements.*

498. First of all, it is important to notice that *the properties of the elements simply differ in quantity, not in quality* or in kind. This is true for their chemical as well as for their physical properties. The more progress we have made in the knowledge of any one property, the more completely this property was recognized as simply varying in *quantity.* This is the case with density, specific heat, and with chemical combining power (atomicity) and affinity (caloration). The table of **101**, giving what we believe to be a *natural classification* of the elements, presents this simple quantitative difference in regard to the atomic weight and atomicity.

499. If, then, we assume, as a hypothesis, that there is but *one matter, of which the elements are polymeric modifications* (see 169), can we obtain, theoretically, a sufficient number of firmly established consequences of this hypothesis, which may enable us to test this hypothesis by experience?

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* Formerly, the nature of the interior of the earth — whether hollow, empty, filled with fire or with molten metal, or solid, — was likewise a matter of speculation. In the progress of science, the theoretical answer has been made: it is not empty, but filled with *dense* matter, probably metallic. The experimental answer to that question probably never will be obtained.

500. The *first* consequence necessarily is, that *the atomic weights of the elements should be exact multiples of the atomic weight of this primary matter*, which, for the sake of brevity, we might call *pantogen*, and denote its atomic weight by p. So far as experiments have been made, this is the case, and p is probably one-half — that is, *each atom of hydrogen consists of two atoms of pantogen.* The very careful determinations of the atomic weight of elements made by *Stas* do not affect this conclusion, because they undoubtedly indicate some disturbing cause which, to a slight extent, affects the weight of molecules.* To deny the existence of a common multiple of the atomic weights to-day, is exactly the same as would have been the denial of *Kepler's Laws*, if the methods of astronomical observarion had attained their present high degree of perfection, while theoretical astronomy had remained stationary since the days of Kepler.

501. We are therefore warranted to test the hypothesis further. The next most general feature of the elements is, evidently, their distribution into almost parallel groups (*genera*) of definite atomicity. Thus, the first three members of three genera of metalloids — oxygen, nitrogen, and carbon — evidently decrease two units in atomic weight as the atomicity increases one unit (see 101). If we generalize this, we can express the atomic weight, a, of these elements by the formula —

$$a = 2(10 - n) = 20 - 2.n,$$

where n is the atomicity. This gives for —

Atomicity, n =	1	2	3	4
Atomic weight, a =	18	16	14	12
Observed,†	Fl-1	O	N	C

502. Now this corresponds exactly to the organic or complex radicals — namely, if we start from the saturated methane, $CH_4 = 16$, we have $a = 16 - n$, namely:

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* As shown in my fourth "Contribntiou to Molecular Science," 1870, pp. 57 to 59.

† Since fluorine is comparatively less known, its deviation is of least importance. The three thoroughly known elements *agree* with this calculation.

Atomicity............ n =	1	2	3	4
Atomic weight...... a =	15	14	13	12
Radicals....................	CH_3	CH_2	CH	C

It is evident that the graphical symbols (Fig. 1, line F,) might completely represent the above four elements, if the dot stands for two—*i. e.*, four pantogen atoms, probably a small tetrahedron (Chem. p. 128)—while the cross stands for twelve, some aggregation of pantogen atoms in the shape of a square prism from one end of which the four corners have been removed. It will be seen that this not only accounts for the atomic weight, but also for the atomicity of these most important elements.

503. Now the *sulphoid* elements can all be considered as polymers of oxygen — of course, not in the common manner, but more closely united; for, *arithmetically*, $S = 32 = 2.O$; $Se = 80 = 5.O$; $Te = 128 = 8.O$, where $O = 16$. It is, however, more likely that the sulphur atom simply is twice as long (or as broad) as the oxygen atom; that the Se and Te atoms result from the addition of three additional aggregations of the weight, sixteen each, as indicated in Fig. 41. It will be noticed that this is in harmony with the formation of amines (191) and with the laws of crystallization (460 to 468).

504. It will be seen that the second member in each of the four genera very nearly corresponds in weight to the first *plus* the same increment sixteen. Thus, $Fl + 16 = 35$, while $Cl = 35.5$; $N + 16 = 30$, while $P = 31$; $O + 16 = 32 = S$; $C + 16 = 28 = Si$. These differences have, undoubtedly, their cause in some special form of aggregation yet unknown; but the relations are too general to be overlooked.

505. For the higher members of these genera, the atomic weights calculated by the addition of 3.16, 3.16 and 6.16, which gives the weight of the consecutive sulphoids, gives values too great—probably because in the actual aggregation certain portions are absent to give points of attraction (atomicities) for the holding together of the atom.

506. The best characterized group of metals, the *kaloids*, exhibit in their atomicity, and in their atomic weight undoubted traces of their atoms being simple aggregations of pantogen-atoms. Thus, suppose that the atomic weight four form a square; then two such squares superposed, weigh eight, but have no atomicity. The removal of one corner leaves the prism (Fig. 42), which has one point of attraction, or is monatomic; its weight is $7 = \mathrm{Li}$. If now the complete lower square grows by the aggregation of a like square (of weight four) to each of its sides, the new atom resulting weighs $7 + 4 \times 4 = 23 = \mathrm{Na}$. By four additional squares of weight four each, this lower plate now will be completed; the resulting atom will weigh $23 + 4 \times 4 = 39 = \mathrm{Ka}$. Thus, the observed atomicity and atomic weight of the kaloids is certainly in harmony with the simplest laws of quadratic aggregation. By a like addition of 3.16, we obtain $39 + 3 \times 16 = 85$, and $85 + 3 \times 16 = 135$, almost the observed atomic weights of the new metals, rubidium, $\mathrm{Rb} = 85.4$, and Cæsium, $\mathrm{Cs} = 133$.

507. The relations here given might be extended to other genera of elements, with more or less accuracy; but what has been given suffices to show that, for the most characteristic and best known elements, the atomicity and atomic weight is such as would result from some simple aggregation of a primary matter, pantogen. Of course, this does not completely demonstrate that such *is* the constitution of the elements, and that pantogen really exists; but it is at least highly probable that the elements are so constituted, and therefore not really simple.*

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* In our *Atomechanik* (1867), we have tried to show that the physical properties also do indicate a composite nature of the element-atoms. The first comparisons of the element-atoms to complex radicals are due to *Dumas* (1857), but he referred exclusively to the atomic weight of elements of similar character. Since we above have combined this with the atomicity and the general laws of aggregation, we believe that whhat here has been given is more conclusive, especially as we have shown that the slight deviations of *Stas* have all the essential characters of secondary perturbations.

PART II.

SYSTEMATIC CHEMISTRY.

508. *Systematic Chemistry comprises a short description of the most important chemical compounds, in systematic order.*

509. As a model of this branch of chemistry, we may here refer to our *Descriptive Mineralogy* (Chem. pp. 129–155), which is the systematic chemistry of native inorganic compounds.

510. In Part I. we have already (in Sections VI., VII., IX., X., and XII.,) given the complete *outline* of systematic chemistry, so that the student may work up any given topic of systematic chemistry during the "*review*" of Part I.

511. That is, if Part I. has been properly presented in lectures by the professor, exhibiting and describing typical compounds of each kind, then during the review of Part I. the student must be required to submit to the professor a *written synopsis* on certain groups of compounds. Of course, different students of a class should treat of different groups. They should give proper references to the sections or pages of the "Elements of Chemistry" or to these "Principles," and besides be encouraged to use the "reference library" of the laboratory.

512. As topics suitable for *one* student, may be assigned the following: the phosphoids; the bromides; the cyanates; the chloroplatinates; the formates; the xylols; the opium alkaloids. A like series of topics, ranging from the elements to the complex compounds, should be assigned to each student.

513. At the same time, the student should, in his laboratory work, be required *to prepare a number of specimens* exemplifying either one series of compounds, or some of the most important compounds of the different groups assigned to him. It need not be accentuated that these preparations are profitably combined with the laboratory work of 29 to 34, 402, 429, and many others. The specimens should be pure, and put up in labelled specimen tubes. (Phys. 164.)

514. As a general form for the description of each compound, may be adopted the following:

1. *Name* (with *synonyms*);
2. *Formula;*
3. *Properties* — physical, chemical (pyrognostic* and hydrognostic†), and physiological;
4. *Occurrence* (as in mineral or in organic beings);
5. *Preparation* — from its raw materials;
6. *Uses* — in science, arts, as medicine, etc.;
7. *Statistics* — in regard to production and consumption;
8. *History.*

Of course, only the most important substances are expected to be thus fully treated of. In general, the chemical *analytical* properties ought to be omitted in case *Qualitative Chemical Analysis* has not yet been studied by the student. (See note to 519.)

515. In the case of students who have not time enough for the careful study of this subject, it will have to be sufficient to give an *oral review* on the subject of systematic chemistry, limited to those facts treated of in the "Elements" and "Principles" of Chemistry. For such a review, the older and less scientific classification according to the electro-positive element may be followed — that is, the topics of *iron* and its compounds, *sodium* and its compounds, etc., etc., may be selected. In organic chemistry, the example of Section VII. corresponds to this mode of exposition. Since nearly all chemical manuals are constructed on this plan, the student may in a short time look up any of these topics.

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* Dry way.(Chem. 116).

† Wet way — deportment of the compound towards solvents and reagents.

516. The field of systematic chemistry is so large, that the general student cannot do more than make himself acquainted with a few prominent series of compounds, as indicated. Whenever he afterwards desires to use information in regard to any point not studied by him, he will be *qualified* to make use of any of the many *reference works* of chemical literature.

517. We are confident that if these suggestions are intelligently and faithfully carried out by teacher and pupil, the latter will have acquired a far better knowledge of systematic chemistry than he could gather from a special volume on this subject placed in his hands.

PART III.

APPLIED CHEMISTRY.

518. *Applied Chemistry treats of the applications of chemistry in the Arts.*

This definition is sufficient to show that also this part of the principles of chemistry can only be treated in a *suggestive* manner in a manual intended for the general student (4).

519. The mere enumeration of the principal branches of applied chemistry would fill a number of pages. The *one* branch of applied chemistry of greatest interest to nearly all students is *Chemical Analysis;* but this again necessarily sub-divides into *qualitative* and *quantitive analysis;* and each of these branches is again so great a field of study that a division and corresponding selection becomes necessary. Thus, qualitative chemical analysis comprises general qualitative chemical analysis in the dry and the wet way,* chemical determination of minerals, the detection of poisons (toxicology), the examination of waters and of foods, the examination of urine (urine-analysis) and of milk, blood, etc., etc. Similarly, quantitative chemical analysis embraces general gravimetric analysis, volumetric analysis, assaying, etc., etc.

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* A practical guide of *qualitative analysis* we have had in preparation for a number of years. We use, during the instruction, minute quantities of normal solutions with the happiest results. The study of general qualitative analysis may most conveniently precede the "Principles" and follow the "Elements" of Chemistry.

520. The application of chemistry to the smelting of metals from their ores (*metallurgy*), the manufacture of chemicals, of drugs, etc., etc., constitute additional great branches of chemical science. Besides, chemistry is applied to physiology, in agriculture, etc. — as shown by special treatises on *Physiological Chemistry*, on *Agricultural Chemistry*, etc. The operations of preserving and cooking food, the purification and disinfection of water and air, the embalming of corpses, ought also to be represented in a treatise on applied chemistry. Finally, the great phenomena of the world around us — in the rocks, the ocean, the atmosphere, and even in the distant planets and stars — have been chemically investigated, as is shown in *Cosmical Chemistry.*

521. It is evident that applied chemistry cannot be mastered by any one man, and that the *general student*, for whom these principles are intended, can only study a few of the simple processes, by way of *example.* The teacher should assign the topic, and give references and necessary assistance. The latter will not need to be very extended, if the student has properly mastered the elements and principles of general chemistry.

522. Concerning the great chemical industries, or *Technical Chemistry* proper, we may add the following general principles:

Since the only immediate aim is the *making of money*, the questions of *economy* dominate in all processes, and require —

a. *The least transportation* of raw materials, especially the more bulky — such as fluxes, fuel, water.

b. *The least direct handling at the works* — making each process as near as possible continuous, moving and stirring masses by machinery and on rails, etc.

c. *Greatest utilization of waste products*, by reproducing the used agent (regeneration of sulphur in the soda process) and by the erection of accessory works (bleaching powder manufactured from waste hydrogen chloride in soda process).

d. *Highest development of the marketable product*—*i. e.*, production of steel and rolled zinc, rather than pig iron or spelter.

e. *Combination of capital*, so as to carry on the processes on the largest possible scale.

523. The question of *profit* is, by competition, brought down to a very narrow margin, where the struggle for existence will develop: *a*, *protection* by goverment against *foreign* competition (as at present in the United States); *b*, a depression of the wages of the laborer (*cheap labor*), most readily in densely populated countries (England); *c*, a *rational and progressive development*, based upon skilled labor and trained experts, prepared in technical and polytechnic schools (illustrated by the marvelous industrial development of Germany during the last thirty years). May the men who "run" some of the industrial universities established by the liberality of Congress soon learn that to "make ink" and the like, is simply a crude imitation of the lowest forms of apprenticeship — not the training of rational technicians.

524. In conclusion, we then recommend the teacher to lecture on a few special technico-chemical processes which are familiar to him, and which are practiced in technical works at a distance which may be conveniently reached by a majority of the students on an *excursion.* Besides, some of the students may substitute some technical topic for one of the topics of systematic chemistry.

525. Since, then, examples will be determined by the opportunities of the teacher and other special causes, it is impossible, in a general treatise, to give more than these *suggestions* in regard to the subject of Applied Chemistry. If the student has mastered the "Elements" and "Principles" of Chemistry, he is ready to pursue *any* special topic of chemistry which may come in his way.

APPENDIX.

526. To the preceding directions (508 to 525) only a few remarks (9) need be added in regard to the work which college students should perform in connection with the study of this little volume.

527. The least that can be demanded of the *classical student* in college is the *numerical solution* of some of the many problems connected with this work. A great many such problems are indicated in the following articles: 19, 24, 29, 42 (e), 45, 52, 53, 54, 85, 86, 145, 314, 336, 348, 359, 377, 380, 413, 416, 436, 436, 441, 450, and others.

The student of abstract mathematics should observe that all experimental data are concrete numbers, known with a certain degree of precision. Hence, it is evidently worse than absurd to calculate or retain more digits and decimals than correspond to this degree of precision; for if *more* are given, they are necessarily false. *Ordinarily*, only *three* or *four* significant digits can be relied on in these cases; hence, *four-place logarithms* are abundantly sufficient for all problems here indicated.

In order to avoid the introduction of error by calculation, it is customary to retain one more place of decimals than absolutely certain.

528. The use of four-place logarithms is especially useful in the calculation of percentage and formulæ, and in the reduction of gasometric experiments (see 52 to 54).

Thus, the molecular volume, v, (in cc.) of any gas is, at the absolute temperature $T = 273 + t° C$, and under the pressure of p mm. (see 52) —

$$\log v = 1.5091 + \log T - \log p.$$

The weight, W, of a volume, V, cc. (at t° C and p mm.) of any gas, the molecular weight, w, of which is known, is (see 54), in milligrams —

$$\log W = \log w - 1.5091 + \log p - \log T + \log V.$$

If the gas stands over water, then the pressure, h, of the aqueous vapor must be subtracted from the total observed pressure in order to get p in this formula. Observation gives —

for	0		5		10		15		20		25		30	degrees C,
pressure, h:	4.6		6.5		9.1		12.7		17.4		23.6		31.6	mm. mercury
incr. for 1°:		0.6		0.5		0.7		0.9		1.2		1.6		mm.

529. The *scientific student* in college will not need to solve many of these problems by simple data given him; for he will perform the experiments himself, and become well trained in calculation by the reduction of his own observations.

The simplest experiments are those indicated in the following articles: 24*, 25, 33, 34, 56, 331, 239, 269, 270, 224, 225, 185, note, etc., etc. This series of experiments may be indefinitely extended, according to the time of the student, and the laboratory facilities at disposition.

For special students in chemistry, we would recommend to precede the study of these "Principles" by a course of qualitative analysis (see 519, note), and to work a great number of *quantitative* experiments in these "Principles," which thus will give training in gravimetric, volumetric, and gasometric analysis. Of course, a great amount of work may also be done in organic chemistry. The professor and the reference library will guide the student in this laboratory work.

530. In conclusion, the following

ERRATA AND ADDENDA

will be necessary:

The table of atomic weights, article 101, p. 39, was not corrected according to latest determinations; hence, please correct the atomic weights of Zn, Au, Pd, Pt, Bi, and the misprint in Se, according to the values of 18, p. 6.

The area required for the culture of madder has been grossly over-stated in the foot-note to page 105. One acre produces about *fifteen tons* of the root; hence, three hundred and twelve acres will supply Lancashire, and sixteen thousand acres will supply all England.

Only in the second series of the diatomic acids of article 206 will the two hydrogen radicals be replaced by two strong basic radicals; so that only this series is truly bibasic — it contains $2CO$.

In the formula of trichloracetic acid, article 133, erase the second H. As clearly shown by context and name, it is HOC_2Cl_3O.

In article 214, read $C_{10}H_{16}O$, instead of $C_{10}H_{16}$.

In article 96, read FeS_2, instead of Fe_2S.

In article 102, fifth line, read electro-negative, instead of electro-positive.

Whether a diploma is printed on true "sheep-skin" or on papyrin (see 246), can be determined by burning a small strip of the same. The odor of burnt hair shows that it is animal, and not papyrin.

The *absolute* value of the moment of inertia of ethers (344) will not be known until the *stereoographic* formula of these compounds has been obtained (158 and 159), at least so far as the position of the two radicals is concerned.

The molecular weight of *potassium* has recently been experimentally determined to be Ka_2 — thus giving a most important confirmation of Avogadro's Law. (Compare 59 and 66).

THE DESCRIPTION OF THE FIGURES

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ASTOR, LENOX AND
TILDEN FOUNDATIONS.

Plate I.

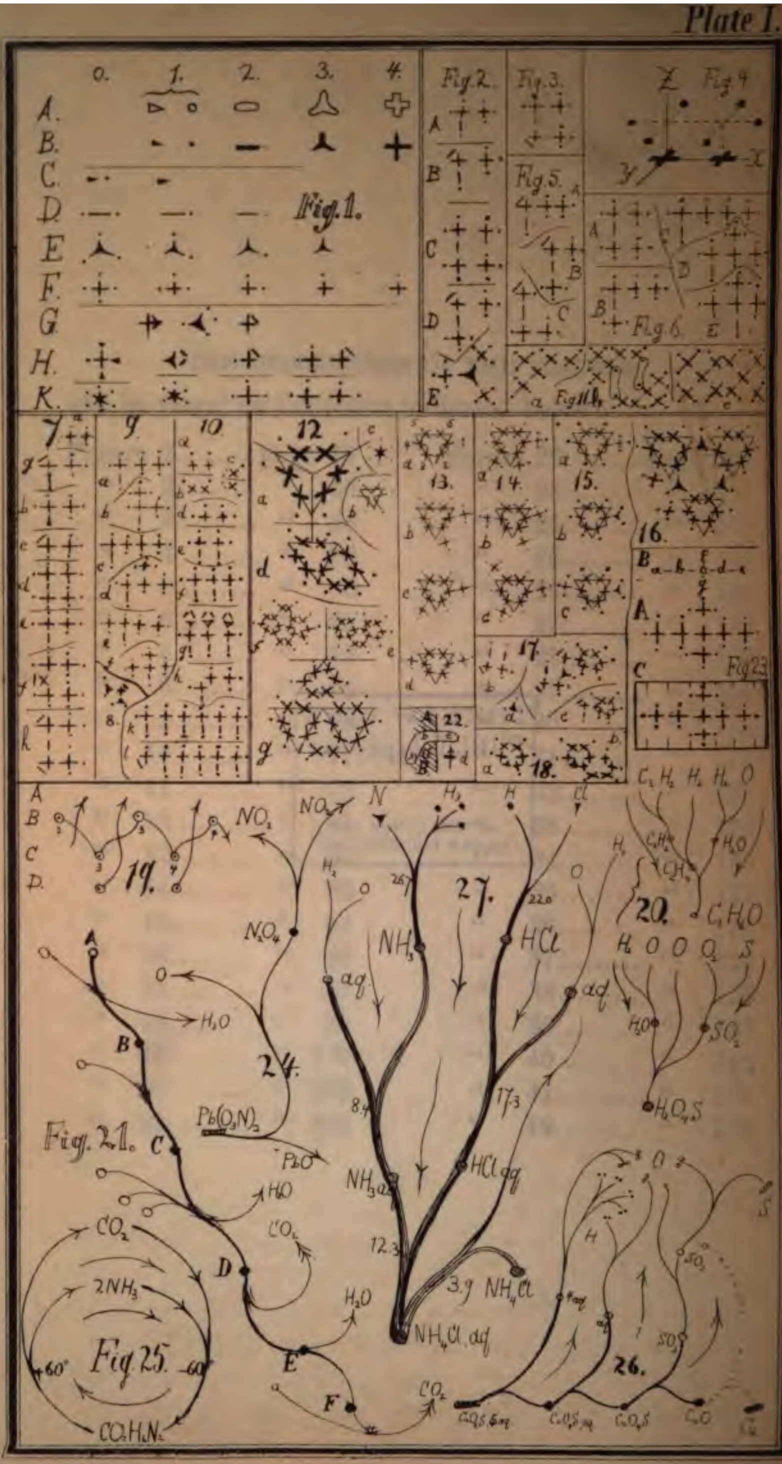
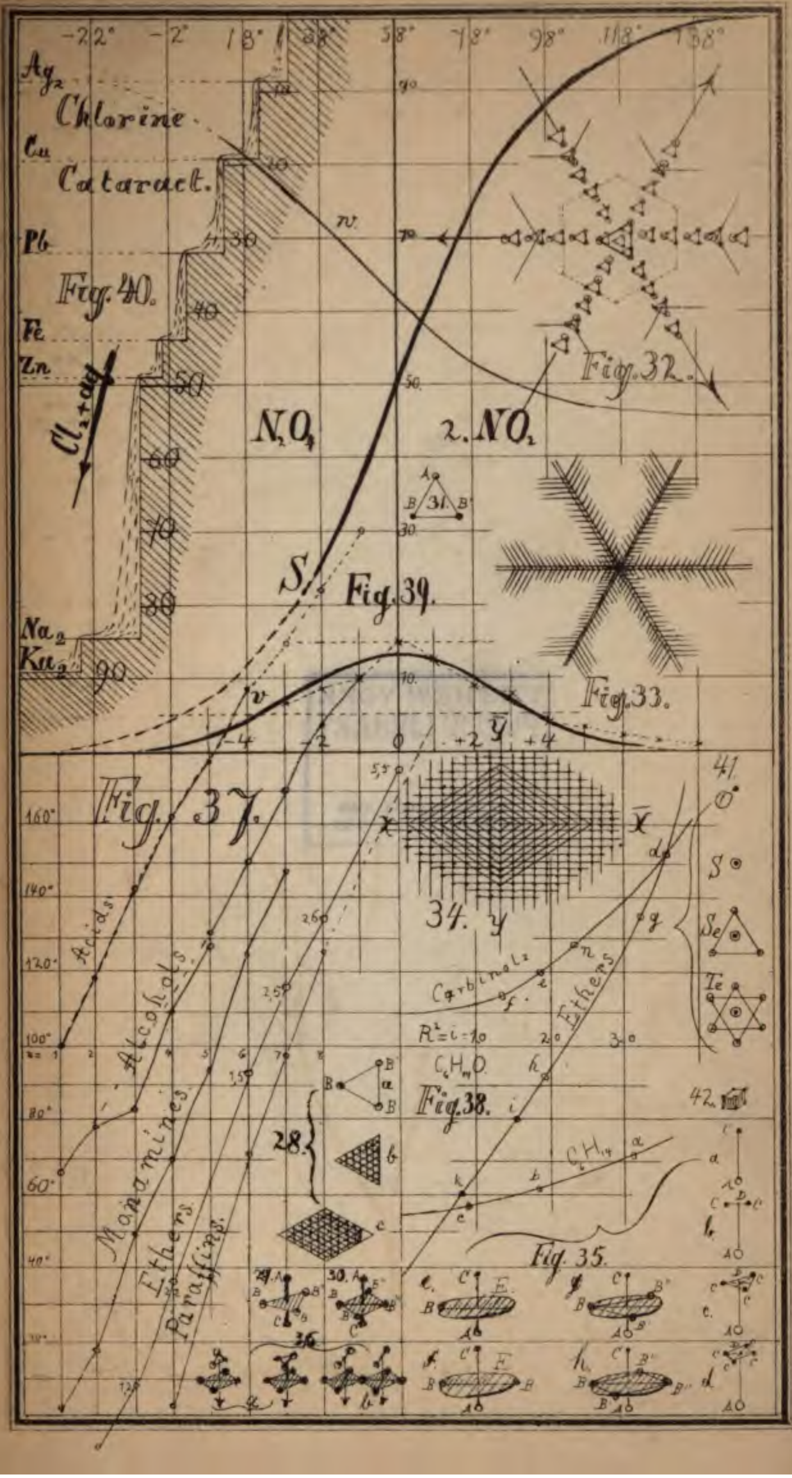


Fig. 1.
0. 1. 2. 3. 4.
A. B. C. D. E. F. G. H. K.
Fig. 2.
Fig. 3.
Fig. 4
Z X Y
Fig. 5.
Fig. 6.
Fig 11
7. 8. 9. 10. 12. 13. 14. 15. 16. 17. 18. 22.
Fig. 23
19.
20.
C_1H_2 H_2 H_2 O
C_1H_2
H_2O
C_2H_6
C_1H_2O
H O O O_2 S
H_2O
SO_2
H_2O_4S
Fig. 21.
A B C D E F
H_2O
CO
CO_2
24.
NO_2
N_2O_4
O
$Pb(O_3N)_2$
PbO
Fig. 25.
CO_2
$2NH_3$
60°
$CO_2H_4N_2$
26.
O
S
H
SO_2
C_2O_4S
C_2O
27.
N
H_3
H
Cl
H_2
O
NH_3
HCl
aq
aq
26.7
22.0
8.4
17.3
NH_3 aq
HCl aq
12.3
3.9
NH_4Cl
NH_4Cl, aq

Plate II.


-22° -2° 18° 38° 58° 78° 98° 118° 138°
Ag₂
Chlorine
Cu
Cataract.
Pb
Fig. 40.
Fe
Zn
Cl₂ + aq
Na₂
Ka₂
10 20 30 40 50 60 70 80 90
w.
Fig. 32.
N₂O₄
2. NO₂
A B 31. B′
S.
Fig. 39.
Fig. 33.
v
-4 -2 0 +2 +4
y
Fig. 37.
160° 140° 120° 100° 80° 60° 40° 20°
n = 1 2 3 4 5 6 7 8
Acids.
Alcohols.
Monamines.
Ethers.
Paraffins.
x x
34. y
41
O S Se Te
Carbinols
Ethers
d g n e f h i k c b a
R² = i = 1.0 2.0 3.0
C₆H₁₄O.
Fig. 38.
C₆H₁₄
28. a b c
B B′ B
42.
Fig. 35.
29. 30. 36 a b
e. f. g. h. c. d.
A B B′ B″ C E F

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